

Correlation and Prediction of Acid Gases Solubility in Various Aqueous Alkanolamine Solutions Using Electrolyte Cubic Square-Well Equation of State

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Abstract

The object of this work is solubility correlation and prediction of CO₂ and H₂S in various aqueous alkanolamines using the electrolyte cubic square-well equation of state (eCSW EoS) (Haghtalab, A., Mazloumi, S. H., (2010), Electrolyte Cubic Square-Well Equation of State for Computation of the Solubility CO₂ and H₂S in Aqueous MDEA Solutions, Ind. Eng. Chem. Res., 49, 6221-623). The eEoS systematically is applied to describe the solubility of acid gases in various alkanolamine solutions, including MDEA, MEA, DEA, AMP, DIPA, TEA, DGA and PZ. In calculations of chemical equilibrium all of the molecular and ionic species have been taken in to account. Also, in order to improve the modeling, the N₂O analogy method was used to calculate the molecular interaction parameters in binary acid gas and alkanolamine solutions. The results of the method are in good agreements with experiments. To investigate the accuracy of the modeling, the simultaneous solubility of mixed CO₂ and H₂S in aqueous MEA, DEA, MDEA, TEA and AMP solutions are also predicted. Acceptable results were achieved for the quaternary systems. In this work, over 3000 experimental data points were used in order to correlate and predict the solubility of CO₂ and H₂S in the various alkanolamine solutions.

Keywords

Modeling, Alkanolamines, Acid gas solubility, N₂O analogy, Electrolyte CSW EoS

1. Introduction

Acid gas impurities such as CO₂ and H₂S must be reduced or even removed from natural gas, because existence of these gases causes some industrial and environmental problems such as equipment corrosion, environment pollution and etc. The chemical absorption methods using alkanolamines are widely used for removal of these impurities from gas flow. Along with the experimental works, thermodynamic modeling is a useful and necessary tool in design of the processes. In literature many models have been presented to correlate and predict the acid gas solubility in alkanolamine solutions. These models may be divided in three categories. The first is empirical models. In these models, the activity coefficients of all species are assumed to be

equal to unity. The fitting parameters are the equilibrium constants. The model of (Kent & Eisenberg, 1976) is one of the well-known models, which is commonly used by process engineers because of having low complexity and low computational effort. Another method is excess Gibbs energy model in which an activity coefficient model is used to describe the nonideality of the liquid phase. These models usually consist of two or three terms. One of these terms is normally based on the Debye-Huckel expression or its extensions, which used for the contribution of long range interactions. The Born term may be added to represent the contribution of mixed solvents effects. Also for the nonidealities of the vapor phase, an equation of state (EoS) may be used. The method has been well established and implemented by several authors. The most

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important weakness of these types of models is that the pressure effect on the activity coefficient has not usually been taken into account. Also Henry's constants for solubility of the fugacious components, such as acid gases, should be available. (Deshmukh & Mather, 1981), (Clegg & Pitzer, 1992), (David M. Austgen, Rochelle, Peng, & Chen, 1989), (Ali Haghtalab & Tafti, 2007), (Ali Haghtalab & Shojaeian, 2010) and (Alhseinat, Mota-Martinez, Peters, & Banat, 2014) are some example works in this category.

The third method is based on $\varphi - \varphi$ approach in which an EoS models is used to represent the nonideality of the liquid and vapor phases. This approach that is almost new technique for computations of solubility of acid gases in alkanolamine solutions, is not subjected to the mentioned weakness. In recent years, the application of a suitable EoS for computation of a VLE of alkanolamine systems is an interesting topic. However, the published papers on this approach are more limited than the previous approach (Fürst & Planche, 1997) have used two different EoSs, one for liquid phase and one for vapor phase, in order to calculate solubility of the acid gases in alkanolamine mixtures. (Kuranov, Rumpf, Maurer, & Smirnova, 1997) and (Smirnova, Victorov, & Kuranov, 1998) have applied the hole model and SRK EoS for representation of the vapor-liquid equilibrium in the alkanolamine solutions. (Vallée, Mougin, Jullian, & Fürst, 1999) have studied the solubility of acid gases in aqueous DEA solution. They used the electrolyte EoS which was developed by (Fürst & Renon, 1993). The same eEoS has been also used by (Chunxi & Fürst, 2000) in order to study the solubility of acid gases in aqueous MDEA solutions. (Fürst & Renon, 1993) eEoS have been adopted to represent the solubility of CO_2 in aqueous piperazine solutions by (P. W. Derks, Dijkstra, Hogendoorn, & Versteeg, 2005). For computation of the VLE of the quaternary $\text{CH}_4 - \text{CO}_2 - \text{MDEA} - \text{H}_2\text{O}$ and $\text{CH}_4 - \text{H}_2\text{S} - \text{MDEA} - \text{H}_2\text{O}$ systems, the Born term was added to (Fürst & Renon, 1993) eEoS in order to improve the modeling by (P J G Huttenhuis, Agrawal, Solbraa, & Versteeg, 2008; P J G Huttenhuis, Agrawal, & Versteeg, 2008). They also extended the eEoS to represent the mixed $\text{CO}_2, \text{H}_2\text{S}$ and CH_4 in the aqueous MDEA solution (P. J. G. Huttenhuis, Agrawal, & Versteeg, 2009). (Ali Haghtalab & Seyed Hossein Mazloumi, 2009) have used eCSW EOS for correlation of the solubility of CO_2 and H_2S in aqueous MDEA solutions in a wide

range of acid gas loading, temperature, and pressure (Ali Haghtalab & Mazloumi, 2010). They have been also predicted the solubility of mixed acid gases in aqueous alkanolamine solution. (Zoghi, Feyzi, & Dehghani, 2012) have applied mPR-CPA EoS for representation of the VLE in the $\text{CO}_2 - \text{MDEA} - \text{H}_2\text{O}$ system.

The aim of the present work is to correlate and predict the solubility of acid gases in various alkanolamine solutions using the eCSW EoS (A. Haghtalab & S. H. Mazloumi, 2009). (Ali Haghtalab & Mazloumi, 2010) have assumed that the effects of second dissociation of acid gases are negligible. Also they did not compute the binary interaction parameters in binaries $\text{CO}_2 - \text{H}_2\text{O}$ and $\text{H}_2\text{S} - \text{MDEA}$. In this work, all of the molecular and ionic species are considered in calculations of chemical equilibrium. In addition, using N_2O analogy approach, the effect of acid gases in alkanolamine in binary systems is calculated in order to improve the modeling of the ternary AcidGas-AMINE-Water systems. In this work, over 3000 experimental data points is used for modeling of solubility of acid gases in various alkanolamine solutions in a wide range of acid gas loadings, temperatures, and pressures.

This work is, in fact, an extension and modification of the previous work of (Ali Haghtalab & Mazloumi, 2010). In this work, some of the simplified assumptions of Haghtalab and Mazloumi such as ignoring second dissociation of acid gases and zero interaction between amine and acid gases have been corrected. Then the modified method has been extended for the various aqueous alkanolamine solutions such as MDEA, PZ, AMP and TEA. So the present model is a reliable thermodynamic method that may be implemented for design and optimization of acid gas sweetening units using alkanolamine solutions.

2. Thermodynamic Framework

2.1. Chemical Equilibrium

When acid gases dissolve in aqueous alkanolamine solutions some equilibrium reactions occur. Thus, chemical equilibrium must be incorporated in the modeling of alkanolamine-acid gas systems due to reactive absorption in liquid phase. (Ali Haghtalab & Mazloumi, 2010) assumed that the effects of second dissociation of acid gases are insignificant, so they did not calculate the effect of CO_3^{2-} and S^{2-} in modeling. Also H_3O^+ and OH^- have not been taken into account. In this work, not only, the second dissociations of

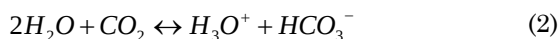
acid gas reactions are considered, but also, the concentration of H_3O^+ and OH^- are involved in computing of chemical equilibrium.

For the $CO_2-AMINE-H_2O$ and $H_2S-AMINE-H_2O$ systems, the following chemical reactions will take place:

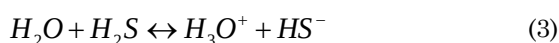
Water dissociation:



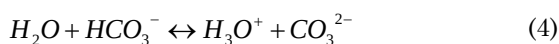
Bicarbonate formation:



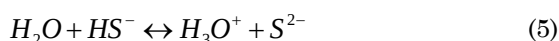
Bisulfide formation:



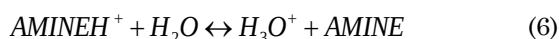
Carbonate formation:



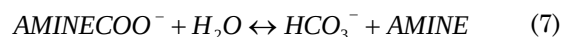
Sulfide formation:



AMINE protonation:



Carbamate formation:



It should be note that the carbamate formation just occurs when the primary and secondary amines have been presented in liquid phase. The dielectric constant for a pure solvent is expressed as:

$$D_s = d_0 + \frac{d_1}{T} + d_2T + d_3T^2 + d_4T^3 \quad (8)$$

where the coefficients of the Eq. (8) are given in table 1. The mole fraction based chemical equilibrium constants of the reactions are expressed as:

$$K = e^{\frac{A+B}{T} + C \ln T + DT} = \prod_i (x_i \gamma_i)^{\nu_i} \quad (9)$$

where x_i is mole fraction, γ_i the activity coefficient, and ν_i the reaction stoichiometry of the species i . The coefficients A, B, C and D are constants that are given in table 2. In this work as in that of (Ali Haghtalab & Mazloumi, 2010), the symmetrical activity coefficient for water is used:

$$\gamma_{Water} = \frac{\varphi_{Water}(T, P, x)}{\varphi_{Water}^0(T, P, x_{Water} \rightarrow 1)} \quad (10)$$

Table 1. Dielectric Constants of Pure Solvents

Solvent	d_0	d_1	d_2	$10^5 d_3$	$10^7 d_4$	Ref
H_2O	-19.291	29815	0.019678	13.189	-3.1144	(Maryot & Smith, 1951)
MEA	-18.5843	14836	0	0	0	(Fang-Yuan Jou, Otto, & Mather, 1994)
DEA	61.7172	0	-0.136743	4.943303	0	(Hsieh, Chen, & Li, 2007)
TEA	103.221	0	-0.37311	38.0795	0	(Hsieh et al., 2007)
DGA	61.7172	0	-0.136743	4.943303	0	(Hsieh et al., 2007)
DIPA	28.8244	0	-0.07191	-7.4526	0	(Hsieh et al., 2007)
AMP	51.2299	0	-0.113191	3.98317	0	(Hsieh et al., 2007)
MDEA	-8.16976	8989.3	0	0	0	(Chunxi & Fürst, 2000)
PZ	148.9	0	-0.62491	77.1	0	(Mazloumi et al., 2012)

Table 2. Chemical Reactions and Coefficients of Equilibrium Constants of the Reactions

Reactions	A	B	C	D	T(K)	Ref
$2H_2O \leftrightarrow H_3O^+ + OH^-$	132.899	-13445.9	-22.4773	0	273-498	(Posey & Rochelle, 1997)
$CO_2 + 2H_2O \leftrightarrow H_3O^+ + HCO_3^-$	213.465	-12092.1	-36.7816	0	273-498	(Posey & Rochelle, 1997)
$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-}$	216.049	-12431.7	-35.4819	0	273-498	(Posey & Rochelle, 1997)
$H_2S + H_2O \leftrightarrow H_3O^+ + HS^-$	214.582	12995.4	-33.5471	0	287-423	(David M Austgen, Rochelle, & Chen, 1991)
$HS^- + H_2O \leftrightarrow H_3O^+ + S^{2-}$	-32.0	-3338.0	0	0	287-343	(David M Austgen et al., 1991)
$MDEAH^+ + H_2O \leftrightarrow MDEA + H_3O^+$	-77.262	-1116.5	10.06	0	278-423	(P.J.G. Huttenhuis, Agrawal, Hogendoorn, & Versteeg, 2007)
$TEAH^+ + H_2O \leftrightarrow TEA + H_3O^+$	-10.6518	-3088.69	0	0.010517	273-323	(Y.-g. Li & Mather, 1996)
$MEA H^+ + H_2O \leftrightarrow MEA + H_3O^+$	-4.90736	-6166.1156	0	-0.0009848	273-323	(L. B. Lee, 1996)
$HCO_3^- + MEA \leftrightarrow H_2O + MEACOO^-$	0.030669	-2275.1900	0	0	298-393	(L. B. Lee, 1996)
$DEAH^+ + H_2O \leftrightarrow DEA + H_3O^+$	-13.2964	-4214.0671	0	0.0099612	273-323	(L. B. Lee, 1996)
$HCO_3^- + DEA \leftrightarrow H_2O + DEACOO^-$	1.655469	-2057.4377	0	0	298-393	(L. B. Lee, 1996)
$AMPH^+ + H_2O \leftrightarrow AMP + H_3O^+$	142.58612	-7261.78	-22.4773	0	Not reported	(Silkenbaumer, Rumpf, & Lichtenthaler, 1998)
$HCO_3^- + AMP \leftrightarrow H_2O + AMPCOO^-$	-11.555	2546.6	0	0	Not reported	(Silkenbaumer et al., 1998)
$DIPAH^+ + H_2O \leftrightarrow DIPA + H_3O^+$	-13.2964	-4214.0671	0	0.0099612	273-323	(L. B. Lee, 1996)
$HCO_3^- + DIPA \leftrightarrow H_2O + DIPACOO^-$	1.655469	-2057.4377	0	0	298-393	(L. B. Lee, 1996)
$DGAH^+ + H_2O \leftrightarrow DGA + H_3O^+$	1.6957	-8431.65	0	-0.005037	Not reported	(D.M. Austgen, 1989)
$HCO_3^- + DGA \leftrightarrow H_2O + DGACOO^-$	-8.8334	5274.4	0	0	298-373	(D.M. Austgen, 1989)
$PZH^+ + H_2O \leftrightarrow PZ + H_3O^+$	18.135	3814.4	0	-0.015096	273-323	(P. W. Derks et al., 2005)
$HCO_3^- + PZ \leftrightarrow H_2O + PZCOO^-$	-4.6185	3616.1	0	0	273-333	(P. W. Derks et al., 2005)

and for the other species with the reference state of infinite dilution in water, the unsymmetrical activity coefficient is used:

$$\gamma_i^* = \frac{\varphi_i(T, P, x)}{\varphi_i^\infty(T, P, x_i \rightarrow 0)} \quad i \neq \text{Water} \quad (11)$$

The eCSW EoS (introduced by details in appendix A.) was used in order to calculate the fugacity coefficient of all component, molecular and ionic species.

2.2. Phase Equilibrium

The eCSW EoS are applied in order to perform the phase equilibrium calculations for molecular components. (Kuranov, Rumpf, Smirnova, & Maurer, 1996) assumed that in the vapor phase only the acid gases and water molecules are present, because alkanolamines

have low vapor pressure in temperature range of 298-413 K. The VLE relation is:

$$x_i \varphi_i^L = y_i \varphi_i^V \quad (12)$$

where x_i and y_i are the mole fraction of component i in the liquid and the vapor phase, respectively. Also, φ_i is the fugacity coefficient of water and acid gas molecules, calculated using the eCSW EoS. In addition to VLE and chemical equations, mass balance equations are needed in order to solve the governing system of equations.

2.3. Mole and Charge Balance

The following mole and charge balance equations are required for the

$CO_2-AMINE-H_2O$ and $H_2S-AMINE-H_2O$ systems.
Water mole balance:

$$n_{H_2O}^0 = n_{H_2O} + n_{OH^-} + n_{HCO_3^-} + n_{HS^-} + n_{CO_3^{2-}} + n_{S^{2-}} \quad (13)$$

Amine mole balance:

$$n_{AMINE}^0 = n_{AMINE} + n_{AMINEH^+} + n_{AMINECOO^-} \quad (14)$$

Acid gases balance:

$$n_{CO_2}^0 = n_{AMINE}^0 \alpha_{CO_2} = n_{CO_2} + n_{HCO_3^-} + n_{AMINECOO^-} + n_{CO_3^{2-}} \quad (15)$$

$$n_{H_2S}^0 = n_{AMINE}^0 \alpha_{H_2S} = n_{H_2S} + n_{HS^-} + n_{S^{2-}} \quad (16)$$

Charge balance:

$$\sum_{i=1}^n n_i Z_i = 0 \quad (17)$$

$$n_{AMINEH^+} + n_{H_3O^+} = n_{OH^-} + n_{AMINECOO^-} + n_{HCO_3^-} + n_{HS^-} + 2n_{CO_3^{2-}} + 2n_{S^{2-}} \quad (18)$$

where α_i , n and Z_i are loading of acid gas i in alkanolamine, the number of moles, and the charge number of ions, respectively. It should be noted that, if the alkanolamine is tertiary amine, the number of moles of $AMINECOO^-$ set equal to zero. to obtain initial moles, the density of pure solvents are needed that are given in table 3. For modeling the $CO_2-AMINE-H_2O$ and $H_2S-AMINE-H_2O$ systems, the mole and charge balance equations and chemical equilibrium equations should be solved simultaneously to obtain the equilibrium concentrations of all components in liquid phase. These equations represent the nonlinear system and in this work, the method of (Smith & Missen, 1988) is used to solve the equations.

Table 3. Density of Pure Solvents

<i>Sol.</i>	<i>Density</i> (gr / cm^3)	<i>Ref</i>
H_2O	$0.999382 + 7.208 \times 10^{-4}(T - 273.15) - 7.2849 \times 10^{-6}(T - 273.15)^2 + 2.65177 \times 10^{-8}(T - 273.15)^3$	(Fang-Yuan Jou et al., 1994)
<i>MEA</i>	$1.0325 - 0.0007979(T - 273.15)$	(Fang-Yuan Jou et al., 1994)
<i>DEA</i>	$0.071689 / 0.23796^{1+(1-T/7366)^{0.2062}}$	(L. B. Lee, 1996)
<i>TEA</i>	$1.134496 - 0.512963 \times 10^{-3}(T - 273.15) - 0.0635384 \times 10^{-5}(T - 273.15)^2$	(Y.-g. Li & Mather, 1996)
* <i>DGA</i>	$0.071689 / 0.23796^{1+(1-T/7366)^{0.2062}}$	(L. B. Lee, 1996)
<i>DIPA</i>	$1.022931 - 0.00076153(T - 273.15)$	(Henni, Hromek, Tontiwachwuthikul, & Chakma, 2003)
<i>AMP</i>	$1.1851 - 0.000853143(T - 273.15)$	(Kundu, Mandal, & Bandyopadhyay, 2003)
<i>MDEA</i>	$1.0553 - 0.0007663(T - 273.15)$	(Abukashabeh, Alhseinat, Al-Asheh, & Bana, 2014)
** <i>PZ</i>	$1.110529 + 0.0055372 C_{PZ} - 3.844 \times 10^{-4} T$	(Peter W. Derks, Hogendoorn, & Versteeg, 2005)

* It is assumed that the density of *DGA* is as same as *DEA*, because of having same molecular weight.

** C_{PZ} concentration of *PZ* in aqueous solution. (mol/lit)

Table 4. Specifications of the Experimental Data Sources Used for the Solubility of Acid Gases in Aqueous MDEA Solution

Author	Wt%	Temp(K)	Loading (mole gas/mole MDEA)	Np
<i>CO₂ – MDEA – H₂O</i>				
(Lemoine, Li, Cadours, Bouallou, & Richon, 2000)	23	298	0.02-0.26	13
(Haji-Sulaiman, Aroua, & Bnamor, 1998)	23, 45	303, 313, 323	0.01-0.88	42
(M. K. Park & Sandall, 2001)	50	298, 323, 348, 373	0.0087-0.4923	30
(Sidi-Boumedine et al., 2004a)	25, 46	298, 313, 348	0.008-1.303	77
(Mamun, Nilsen, & Svendsen, 2005)	50	328, 343, 358	0.1658-0.8133	34
(David M Austgen et al., 1991)	23	313	0.006-0.65	14
(Kuranov et al., 1996)	18, 19, 32	313, 333, 373, 393, 413	0.105-1.157	78
(Rho et al., 1997)	20, 50	323, 348, 373	0.0087-0.8478	58
(Á. P.-S. Kamps et al., 2001)	32, 48	313, 353, 393	0.126-1.243	28
(Rogers, Bullin, & Davison, 1998)	23, 50	313, 323	0.000591-0.1177	34
(Macgregor & Mather, 1991)	23	313	0.124-1.203	5
<i>H₂S – MDEA – H₂O</i>				
(Lemoine et al., 2000)	11,23	298	0.0151-0.2299	27
(Sidi-Boumedine et al., 2004b)	46	313, 373	0.039-1.116	25
(Kuranov et al., 1996)	18,32	313, 333, 373, 393, 413	0.480-1.933	71
(Á. P.-S. Kamps et al., 2001)	48	313, 353, 393	0.153-1.428	26
(Rogers et al., 1998)	23,50	313	0.00627-0.313	22
(Macgregor & Mather, 1991)	23	313	0.382-1.725	18
Total				602

3. Results and Discussion

3.1. The Database

In the present work, in order to validate the model, the experimental database of (Ali Haghtalab & Mazloumi, 2010) for aqueous MDEA was used. For solubility of CO₂ and H₂S in aqueous MEA, the database of many references were studied and agreeing of experiment was reviewed. Since, the discrepancy of various experimental data was slight, so no experimental data was removed. For aqueous DEA, the found of database is same as that of (Vallée et al., 1999) and the

other references were added to the database. For modeling of the solubility of CO₂ and H₂S in these three common solutions (MEA, DEA and MDEA), more than 1600 experimental data points have been used. In table 5, the databases of the experimental data for the solubility of acid gases in MDEA, MEA and DEA solutions have been shown. Also, this table shows the experimental data of the solubility of acid gases in AMP solution. The references of experimental data used in modeling of the solubility of CO₂ and H₂S in aqueous DIPA, TEA, DGA and PZ solutions were given in table 6.

Table 5. Specifications of the Experimental Data Sources Used for the Solubility of Acid Gases in Aqueous MEA, DEA and AMP Solutions

Author	Conc. Amine	Temp(K)	Loading (mole gas/mole MEA)	Np
<i>CO₂ – MEA – H₂O</i>				
(Fang-Yuan Jou et al., 1995)	30 Wt%	298-373	0.0117-1.247	80
(Bhairi, 1984)	2.5 M	298-353	0.413-1.325	60
(Lawson & Garst, 1976)	15.2 Wt%	313-373	0.177-0.998	13
(David M Austgen et al., 1991)	2.5 M	313-353	0.267-0.676	8
(Mamun et al., 2005)	30 Wt%	393	0.155-0.3882	19
(J.-Y. Park, Yoon, & Lee, 2003)	10 Wt%	298	0.408-0.913	9
(Jane & Li, 1997)	2.5 M	353	0.172-0.833	6
<i>H₂S – MEA – H₂O</i>				
(Jong Il Lee et al., 1976)	2.5, 5 N	298-393	0.108-1.61	96
(Lawson & Garst, 1976)	15.2 Wt%	313-373	0.0052-1.63	45
(Bhairi, 1984)	2.5 M	298	0.717-1.454	18
Total				337
<i>CO₂ – DEA – H₂O</i>				
(Jong Il Lee et al., 1972)	0.5, 2, 3.5 N	298-373	0.072-2.695	104
(Lawson & Garst, 1976)	25 Wt%	311-380	0.376-1.167	30
(Bhairi, 1984)	0.5, 2 M	298	0.598-2.012	25
(Lal et al., 1985)	2 M	313, 373	0.042-0.3669	44
(Oyeveaar, Fonteln, & Westerterp, 1989)	1-2.5 M	298	0.463-0.736	14
(Dawodu & Meisen, 1994)	4.2 M	373	0.299-0.725	6
(Haji-Sulaiman et al., 1998)	2.4 M	303-313	0.091-0.786	45
(Sidi-Boumedine et al., 2004a)	41.78 Wt%	298, 348	0.021-1.088	24
(Rogers, Bullin, Davison, Frazier, & Marsh, 1997)	20.2 Wt%	323	0.00663-0.2331	14
<i>H₂S – DEA – H₂O</i>				
(Jong Il Lee et al., 1973a)	2,3.5 N	298-373	0.0051-1.76	112
(Jong Il Lee et al., 1973b)	0.5-3.5 N	298-373	0.0050-3.04	166
(Lawson & Garst, 1976)	25 Wt%	313-380	0.0038-1.582	89
Total				673
<i>CO₂ – AMP – H₂O</i>				
(Tontiwachwuthikul, Meisen, & Lim, 1991)	2, 3 M	293-353	0.126-0.96	40
(Kundu et al., 2003)	2-3.4 M	303-323	0.412-0.938	51
(Silkenbaumer et al., 1998)	2.43-6.24 m	313-353	0.1535-1.19465	66
(Jamal, 2002)	20 Wt%	332-378	0.217-0.756	30
(Haji-Sulaiman & Aroua, 1996)	2 M	303-353	0.33-0.60	20
(Yang, Soriano, Caparanga, & Li, 2010)	3 M	313	0.385-0.939	8
(Jane & Li, 1997)	2 M	313	0.432-0.991	8
(Roberts & Mather, 1988)	2, 3 M	313, 373	0.136-1.325	36
(Teng & Mather, 1990)	2 M	313, 343	0.033-1.265	24
<i>H₂S – AMP – H₂O</i>				
(M.-H. Li & Chang, 1994)	30 Wt%	313-373	0.173-0.936	41
(Jane & Li, 1997)	2 M	313	0.618-1.021	9
(Roberts & Mather, 1988)	2 M	313, 373	0.140-1.715	27
Total				360

Table 6. Specifications of the Experimental Data Sources Used for the Solubility of Acid Gases in Aqueous *DIPA*, *TEA*, *DGA* and *PZ* Solutions

Author	Conc. Amine	Temp(K)	Loading (mole gas/mole DIPA)	Np
<i>CO₂ – DIPA – H₂O</i>				
(Isaacs et al., 1977)	2.5 M	313, 373	0.067-1.111	45
<i>H₂S – DIPA – H₂O</i>				
(Isaacs et al., 1977)	2.5 M	313, 373	0.098-1.414	26
(Mazloumi et al., 2012)	2.95 m	313-353	0.58-1.37	23
(Uusi-Kyyny, Dell'Era, Penttilä, Pakkanen, & Alopaeus, 2013)	10-37 Wt%	295-353	0.087-0.932	77
Total				171
<i>CO₂ – TEA – H₂O</i>				
(Cheng, Caparanga, Soriano, & Li, 2010)	30 Wt%	313-373	0.0405-0.5022	30
<i>H₂S – TEA – H₂O</i>				
(Atwood, Arnold, & Kindrick, 1957)	15-50 Wt%	298-333	0.000271-0.531	17
Total				47
<i>CO₂ – DGA – H₂O</i>				
(Martin, Otto, & Mather, 1978)	60 Wt%	323, 373	0.129-0.798	46
(Chen, 1991)	20-60 Wt%	298-333	0.52-1.302	43
<i>H₂S – DGA – H₂O</i>				
(Martin et al., 1978)	60 Wt%	323, 373	0.057-1.091	36
Total				125
<i>CO₂ – PZ – H₂O</i>				
(A. P.-S. Kamps, Xia, & Maurer, 2003)	1.995-3.950 m	313-393	0.501-1.68	92
(P. W. Derks et al., 2005)	0.2, 0.6 M	298-343	0.36-1.23	52
(Ermatchkov et al., 2006)	0.989-4.443 m	313-393	0.0519-0.807	33
<i>H₂S – PZ – H₂O</i>				
(Xia, Kamps, & Maurer, 2003)	2, 4 m	313-393	0.597-2.429	82
(Speyer & Maurer, 2011)	2 m	313	0.520-1.037	25
Total				284

3.2. The Pure Parameters

σ , ε , and λ are the adjustable parameters of the eCSW EoS for pure components. These parameters that are given in Table 7 are calculated by simultaneous optimization of the saturated vapor pressure and the liquid density of the pure components. The parameters of acid gases, water, and *MDEA* were taken from (Ali Haghtalab & Mazloumi, 2010). Also, for *DIPA* and *PZ*, (Mazloumi, Haghtalab, Jalili, & Shokouhi, 2012) have calculated the pure parameters of the CSW EoS. The parameters of the CSW EoS for *MEA*, *DEA*, *TEA*, *DGA*,

AMP, and *DIPA* have been fitted, using the vapor pressure data alone. One should note that for *DIPA* the new parameters are fitted in wider range of temperature than (Mazloumi et al., 2012) work, so that the new parameters of the eCSW presented here, for *DIPA*, are different from those of their paper. However, the parameters of *PZ*, were taken from (Mazloumi et al., 2012). In this work, it is assumed that for the ionic species such as *AMINEH*⁺, *HS*⁻, *HCO*₃⁻ and *AMINECOO*⁻ the parameters of CSW EoS are the same as those of the corresponding molecular species, i.e.,

AMINE, H_2S and CO_2 , except for the diameters of the HCO_3^- and the $AMINECOO^-$. Diameter of HCO_3^- is taken from the literature (P J G Huttenhuis, Agrawal, Solbraa, et al.,

2008). For $AMINECOO^-$, it is assumed that the diameters of these kinds of ions, such as $MEACOO^-$, is equal summation of the diameters of the *AMINE* and the CO_2 .

Table 7. Parameters of the eCSW Equation of State

<i>Species</i>	$\varepsilon / k_{(k)}$	λ	$\sigma(^{\circ}A)$	T_r range	AAD% <i>P</i>	AAD% ρ	<i>Ref</i>
H_2O	772.657	1.4641	2.317	0.44-0.94	5.8	3.5	(Ali Haghtalab & Mazloumi, 2010)
CO_2	462.655	1.3090	2.819	0.77-0.95	0.6	2.2	(Ali Haghtalab & Seyed Hossein Mazloumi, 2009)
H_2S	524.895	1.3330	2.885	0.73-0.96	2.6	1.9	(Ali Haghtalab & Mazloumi, 2010)
<i>MEA</i>	811.075	1.5596	2.202	0.44-0.96	2.2	--	(Avlund, Kontogeorgis, & Michelsen, 2008)
<i>DEA</i>	1066.566	1.5336	2.023	0.43-0.95	0.9	--	(Avlund et al., 2008)
<i>TEA</i>	631.444	2.0702	1.389	0.45-0.92	1.9	--	(Wright, Dollimore, Dunn, & Alexander, 2004)
<i>DGA</i>	558.160	2.0813	0.890	0.44-0.95	7.7	--	(Chen, 1991)
<i>DIPA</i>	1048.417	1.5026	2.235	0.58-0.95	1.6	--	(Uusi-Kyyny et al., 2013)
<i>AMP</i>	536.269	1.8866	1.658	0.45-0.93	0.8	--	(Pappa et al., 2006)
<i>MDEA</i>	1261.451	1.4270	1.692	0.44-0.95	2.3	--	(Ali Haghtalab & Mazloumi, 2010)
<i>PZ</i>	847.891	1.4341	3.384	0.59-0.97	1.4	--	(Mazloumi et al., 2012)
H_3O^+	772.657	1.4641	2.317				
OH^-	772.657	1.4641	2.317				
HCO_3^-	462.655	1.3090	3.120				
CO_3^{2-}	462.655	1.3090	3.120				
HS^-	524.895	1.3330	2.885				
S^{2-}	524.895	1.3330	2.885				
<i>MEAH</i> ⁺	811.075	1.5596	2.202				
<i>MEACOO</i> ⁻	811.075	1.5596	5.021				
<i>DEAH</i> ⁺	1066.566	1.5336	2.023				
<i>DEACOO</i> ⁻	1066.566	1.5336	4.842				
<i>TEAH</i> ⁺	631.444	2.0702	1.389				
<i>DGAH</i> ⁺	558.160	2.0813	0.890				
<i>DGACOO</i> ⁻	558.160	2.0813	4.010				
<i>DIPAH</i> ⁺	1890.666	1.2232	1.633				
<i>DIPACOO</i> ⁻	1890.666	1.2232	4.452				
<i>AMPH</i> ⁺	536.269	1.8866	1.658				
<i>AMPCOO</i> ⁻	536.269	1.8866	4.778				
<i>MDEAH</i> ⁺	1261.451	1.4270	1.692				
<i>PZH</i> ⁺	847.891	1.4341	3.384				
<i>PZCOO</i> ⁻	847.891	1.4341	6.203				

3.3. The Binary Interaction Parameters

Before the ternary systems can be simulated, first the following binary molecular systems k_{ij} have to be studied and optimized. It is assumed that the interaction parameter of binaries in function of temperature is used:

$$k_{ij} = b_1 + \frac{b_2}{T} \quad (19)$$

where T is absolute temperature in kelvin. Three type of adjustable binary molecular interaction parameters exist in the modeling of the solubility of acid gases in alkanolamines. These molecular interaction parameters are as follow.

3.3.1. Acid Gas-Water interaction

For determination of k_{ij} in binaries $\text{CO}_2 - \text{H}_2\text{O}$ and $\text{H}_2\text{S} - \text{H}_2\text{O}$ the data of the solubility of acid gases in water are available in literature. (Ali Haghtalab & Mazloumi, 2010) calculated the solubility of these binary systems in wide range of temperature and pressure. In this work, the interaction parameters of binary systems $\text{CO}_2 - \text{H}_2\text{O}$ and $\text{H}_2\text{S} - \text{H}_2\text{O}$ are taken from their work and shown in table 8.

3.3.2. Alkanolamine-Water Interaction

For determination of k_{ij} in binary $\text{MDEA} - \text{H}_2\text{O}$, (Ali Haghtalab & Mazloumi, 2010), used the interaction energy parameters of the NRTL in order to obtain the activity coefficient data of water, then, they calculated the interaction parameters in binary $\text{MDEA} - \text{H}_2\text{O}$ by eCSW EoS. In this work, for binaries $\text{MEA} - \text{H}_2\text{O}$ and $\text{DEA} - \text{H}_2\text{O}$, following (Ali Haghtalab & Mazloumi, 2010), the binary interaction parameters are determined and the results are given in table 8. As one can see, only the parameter of $\text{DEA} - \text{H}_2\text{O}$ is fitted and for

binaries $\text{MEA} - \text{H}_2\text{O}$ and $\text{MDEA} - \text{H}_2\text{O}$ no experimental data are correlated. The VLE data of the $\text{AMP} - \text{H}_2\text{O}$ system are available in work of (Pappa, Anastasi, & Voutsas, 2006). So the interaction between AMP and water are calculated using eCSW EoS. Also the interaction parameters of binaries $\text{TEA} - \text{H}_2\text{O}$, $\text{DGA} - \text{H}_2\text{O}$, $\text{DIPA} - \text{H}_2\text{O}$ and $\text{PZ} - \text{H}_2\text{O}$ set to be zero.

3.3.3. Alkanolamine-Acid Gas Interaction

In literature, three approach are used to obtain the binary interaction parameters of acid gas in alkanolamine, because there is no available experimental data for the solubility of CO_2 and H_2S in pure alkanolamines. In the first method, as (Solbra, 2002) work, the interaction parameters of alkanolamine-acid gas are calculated by optimization of the solubility of experimental data of acid gases in electrolyte ternary systems. In the second approach, following (Ali Haghtalab & Mazloumi, 2010), the binary interaction parameters of the solubility of CO_2 and H_2S in alkanolamines, are assumed to be zero for the molecular binary systems. In the last approach, N_2O analogy, the experimental data of physical solubility of N_2O in alkanolamines are converted to the physical solubility data of acid gas in alkanolamines. In this work, as work of (P J G Huttenhuis, Agrawal, Solbraa, et al., 2008; P J G Huttenhuis, Agrawal, & Versteeg, 2008), N_2O analogy are applied to determine the binary interaction parameters of CO_2 and H_2S in alkanolamines. In this way, the interaction between alkanolamine and acid gas in the nonreactive ternary system are computed using the interaction parameters of water-alkanolamine and water-acid gas that have been already obtained.

Table 8. Percent of Absolute Average Deviation in Correlation of the Bubble Pressure and in Predicting of Activity Coefficient of Binary Subsystems

system	Trange (K)	k_{ij}		AAD%	Np	Ref
		b_1	b_2			
$\text{CO}_2 - \text{H}_2\text{O}$	313-393	0.3414	-76.56	2.6	39	(Kiepe, Horstmann, Fischer, & Gmehling, 2002)
$\text{H}_2\text{S} - \text{H}_2\text{O}$	298-411	0.2607	-43.87	2.3	53	(Chapoy et al., 2005; Selleck, Carmichael, & Sage, 1952)
$\text{MEA} - \text{H}_2\text{O}$	298-393	0	0	2.1	50	(Chang, Posey, & Rochelle, 1993)
$\text{DEA} - \text{H}_2\text{O}$	298-393	-0.0356	0	1.1	50	(Chang et al., 1993)
$\text{MDEA} - \text{H}_2\text{O}$	298-393	0	0	1.8	50	(Chang et al., 1993)
$\text{AMP} - \text{H}_2\text{O}$	361-436	0	0	12.45	27	(Pappa et al., 2006)

3.3.4. The N_2O Analogy

There are always few amounts of water in pure alkanolamines, so the physical solubility of CO_2 and H_2S cannot be measured directly. The N_2O analogy helped in order to predict the physical solubility in alkanolamines. Acid gases (CO_2 and H_2S) and N_2O are rather similar molecules, but the only difference of them is, N_2O only dissolve physically (not chemically) in alkanolamines. Based on this fact, the physical solubility of acid gas in alkanolamines as term of Henry constant can be computed as:

$$H_{\text{AcidGas-aqueousAMNE}} = \frac{H_{\text{AcidGas-Water}}}{H_{\text{N}_2\text{O-Water}}} \times H_{\text{N}_2\text{O-aqueousAMNE}} \quad (20)$$

It should be pointed out that in the above relation, for determination of physical solubility of acid gas in aqueous alkanolamine solutions, the solubility of acid gas in water, N_2O in water, and N_2O in aqueous alkanolamine solutions are needed. For the solubility of CO_2 and N_2O in water, (P J G Huttenhuis, Agrawal, Solbraa, et al., 2008)

compared the empirical correlation of (Jamal, 2002), and (Versteeg & Van-Swaaij, 1988) with experimental data of (F.-Y. Jou, Carroll, Mather, & Otto, 1992) and their work. They observed that the experimental data are more in line with relation of (Jamal, 2002), so they have used this correlation. In this work, the relation of (Jamal, 2002) was used for prediction the solubility of CO_2 and N_2O in water. Also, for the solubility of H_2S in water, the correlation of (Chapoy, Mohammadi, Tohidi, Valtz, & Richon, 2005) was used. So having the solubility of N_2O in aqueous alkanolamines, the physical solubility of CO_2 and H_2S in alkanolamines is measured. Shown in table 9 is the database of experimental data of several authors that was used for the solubility of N_2O in aqueous MEA, DEA, MDEA, AMP, DIPA, and TEA. One should note that in reference (Abu-Arabi, Tamimi, & Al-Jarrah, 2001) the physical solubility of CO_2 in aqueous TEA solution, has been directly measured by protonation method.

Table 9. Experimental Database for the Solubility of N_2O in Various Alkanolamines

Author	T (K)	Amine Conc. Wt%	np
N_2O–MEA–H_2O			
(Jamal, 2002)	293-393	10-30	24
(M. H. Li & Lai, 1995)	303-313	30.0	3
(Little, Versteeg, & Van-Swaaij, 1992)	303-348	1.1-24.3	30
(Laddha, Diaz, & Danckwerts, 1981)	298	6.7-12.5	2
(Yaghi & Houache, 2008)	293-333	5.0-30.0	30
N_2O–DEA–H_2O			
(Jamal, 2002)	293-393	10.0-30.0	24
(M. H. Li & Lee, 1996)	303-313	30.0	3
(Haimour, 1990)	288-303	10.8-31.7	12
(Little et al., 1992)	303-333	2.6-36.8	23
(Versteeg & Oyevaar, 1989)	298	2.0-80.8	17
(Versteeg & Van-Swaaij, 1988)	298	4.7-31.3	10
(Sada, Kumazawa, & Butt, 1977)	298	4.7-31.3	5
(Laddha et al., 1981)	298	5.2-20.6	3
(Yaghi & Houache, 2008)	293-333	5.0-30.0	30
N_2O–MDEA–H_2O			
(Jamal, 2002)	293-293	10.0-30.0	24
(M. H. Li & Lai, 1995)	303-313	30.0	3
(Al-Ghawas, Hagewiesche, Ruiz-Ibanez, & Sandall, 1989)	298-323	10.0-50.0	35
(Al-Ghawas, Ruiz-Ibanez, & Sandall, 1989)	293-313	15.3-30.2	15
(Versteeg & Van-Swaaij, 1988)	293-333	4.1-31.9	50
(Haimour & Sandall, 1984)	288	10.0-40.0	20
(Pawlak & Zarzycki, 2002)	293	10.0-90.0	8
(M. K. Park & Sandall, 2001)	298-353	50.0	5
N_2O–AMP–H_2O			
(Jamal, 2002)	293-393	10.0-30.0	27
(M. H. Li & Lai, 1995)	303-313	30.0	3
(Saha, Bandyopadhyay, & Biswas, 1993)	288-303	3.5-29.1	24
(Xu, Otto, & Mather, 1991)	283-310	17.8-27.0	8
N_2O–DIPA–H_2O			
(Yaghi & Houache, 2008)	293-333	5.0-30.0	30
CO_2–TEA–H_2O			
(Abu-Arabi et al., 2001)	293-333	10-30	18
Total			486

Figure 1, shows the result of this indirect method for determination of binary interaction parameters of the CO_2 – MDEA – H_2O system. Good agreement observed between experiment (Haimour & Sandall, 1984) and the eCSW model in low and intermediate temperature.

Also, in table 10, the coefficients of Eq. (44) for the binary systems and the percents of average absolute deviation (AAD%) are given. It should be note that for other alkanolamines, such as *PZ* and *DGA*, the interaction parameters of these systems were assumed to be zero.

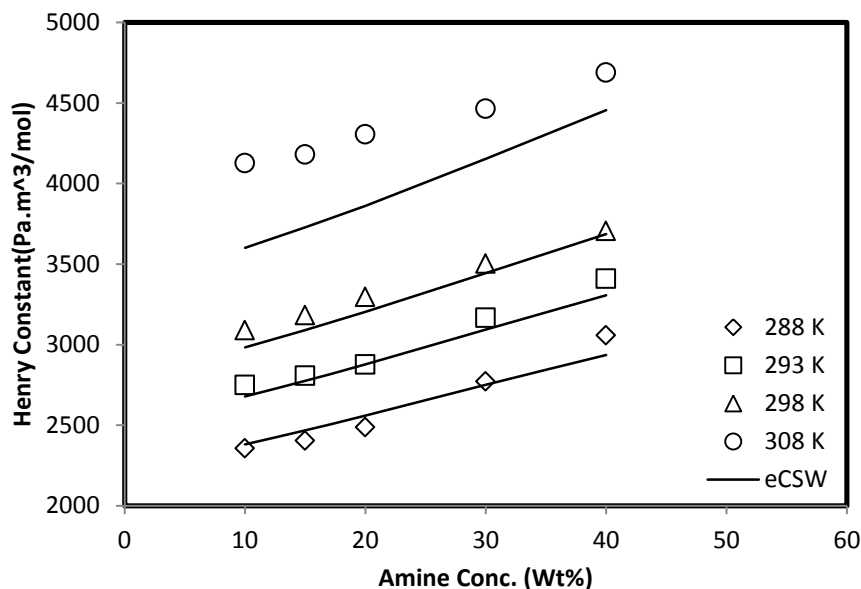


Figure 1. Physical Solubility of CO_2 in Aqueous MDEA at Various Temperatures, the Experimental Data were Taken from (Haimour & Sandall, 1984).

Table 10. Binary Interaction Parameters of Binary Acid Gas-Alkanolamine Systems by Using N_2O Analogy

System	np	$k_{\text{ACIDGAS-AMINE}}$		AAD%
		b_1	b_2	
CO_2 – <i>MEA</i>	89	0.2226	-78.58	4.63
H_2S – <i>MEA</i>	"	0.1603	0.02	12.62
CO_2 – <i>DEA</i>	127	0.0857	0.01	11.35
H_2S – <i>DEA</i>	"	-1.1480	35.39	9.47
CO_2 – <i>MDEA</i>	158	0.2149	-7.89	5.18
H_2S – <i>MDEA</i>	"	-1.234	40.43	8.03
CO_2 – <i>AMP</i>	61	0.1359	-114.60	7.01
H_2S – <i>AMP</i>	"	-.4155	0.06	6.69
CO_2 – <i>DIPA</i>	30	0.2115	-27.24	3.33
H_2S – <i>AMP</i>	"	0.0367	0.00	8.57
CO_2 – <i>TEA</i>	22	-0.0467	3.07	4.98
Total	486			

3.4. The Ternary Systems

The results of the modeling of the solubility of CO_2 and H_2S in the various alkanolamines are presented in this section. The calculation is based on the reactive bubble pressure algorithm that consists of two main loops. The nonlinear mass balance, charge balance and chemical equilibrium equations are solved in internal loop by (Smith & Missen, 1988) approach. The outputs of inner loop are mole fractions of all components in liquid phase that are used for the inputs of external loop. The VLE calculations are carried out in external loop. This procedure continues until the calculations converge. The mole fraction of acid gases and water in liquid phase, and total bubble pressure are the outputs of the algorithm. As discussed in section 2.3., because of low vapor pressure of alkanolamine in the temperature range of 298–413 K, the presence of alkanolamine in the vapor phase is negligible (Kuranov et al., 1996).

In section 3.2., the molecular interaction parameters for binary systems have been already computed and explained, so that the ionic interaction parameters must be optimized using the solubility data of acid gases in the ternary systems of the alkanolamine solutions. It should be pointed out that the binary ionic interaction parameters are temperature dependent through Eq. (44). As it was explained by (Chunxi & Fürst, 2000), the solvation effect of the anion is less than that of the cation, and the interaction between anions and other component present in the liquid phase is negligible. Therefore, it has been assumed that the interactions of the cations with other components have more influence than the interactions of the anion species with other components. Moreover, because the concentration of H_3O^+ is low, the interaction parameters of this cationic specie with other component are ignored (Zoghi et al., 2012). So for the $\text{CO}_2\text{--AMINE--H}_2\text{O}$ system, the ionic binary interactions are:

$$k_{\text{HCO}_3^- \text{--AMINEH}^+}, k_{\text{CO}_3^{2-} \text{--AMINEH}^+}, k_{\text{H}_2\text{O--AMINEH}^+}, \\ k_{\text{OH}^- \text{--AMINEH}^+}, k_{\text{AMINE--AMINEH}^+}, \text{ and } k_{\text{AMINECOO}^- \text{--AMINEH}^+}. \text{ It should be noted that } k_{\text{AMINECOO}^- \text{--AMINEH}^+} \text{ is involved in computation when the alkanolamine is the primary or secondary amine. For the } \text{H}_2\text{S--AMINE--H}_2\text{O} \text{ system, } k_{\text{H}_2\text{S--AMINEH}^+}, k_{\text{HS}^- \text{--AMINEH}^+},$$

$$k_{\text{S}^{2-} \text{--AMINEH}^+}, k_{\text{H}_2\text{O--AMINEH}^+}, k_{\text{OH}^- \text{--AMINEH}^+}$$

and $k_{\text{AMINE--AMINEH}^+}$ are the interactions. As one can observe three interaction parameters are the same in the both ternary systems. In order to have fewer adjustable parameters, the same values for the binary parameters $k_{\text{H}_2\text{O--AMINEH}^+}$,

$k_{\text{OH}^- \text{--AMINEH}^+}$, and $k_{\text{AMINE--AMINEH}^+}$ are considered in both ternary systems. Thus, for modeling of the solubility of CO_2 and H_2S in various alkanolamines, all of the experimental data points of the both ternary systems were used simultaneously, and the binary interaction parameters were fitted. For the solubility of CO_2 and H_2S in aqueous MDEA, the results of the work of (Ali Haghtalab & Mazloumi, 2010) were compared with our work. As mentioned, the difference is that in this work CO_3^{2-} , S^{2-} ,

OH^- and H_3O^+ were involved in the computing of chemical equilibrium. Also, the effect of N_2O analogy on the model for solubility of acid gases in aqueous MDEA was reviewed. In table 11, the comparison of the result of this work and those obtained by (Ali Haghtalab & Mazloumi, 2010), have been shown. They correlated six ionic interaction parameters and used five scenario to calculate the ionic interactions for the $\text{CO}_2\text{--MDEA--H}_2\text{O}$ and the $\text{H}_2\text{S--MDEA--H}_2\text{O}$ systems. In this work, three other ionic interaction parameters are added and correlated; $k_{\text{CO}_3^{2-} \text{--AMINEH}^+}$, $k_{\text{S}^{2-} \text{--AMINEH}^+}$, and

$k_{\text{OH}^- \text{--AMINEH}^+}$. The other ionic interaction parameters for solubility of acid gases in aqueous MDEA are same as those of (Ali Haghtalab & Mazloumi, 2010). The total error was improved by 2 percent in AAD%. Figures 2 and 3, respectively, show the comparison of calculated and experimental (Kuranov et al., 1996) total pressure of the $\text{CO}_2\text{--MDEA--H}_2\text{O}$ and the $\text{H}_2\text{S--MDEA--H}_2\text{O}$ systems in 32.2 wt% concentration of MDEA at various temperature. As one can see the results are more in line with the experimental data. Also, in order to investigate the precision of the result of the concentration of the some species in the liquid phase, Figure 4 shows a comparison of eCSW EoS with the results obtained by NMR study (Jakobsen, Krana, & Svendsen, 2005) at 23 wt% of MDEA and 313 K, for the $\text{CO}_2\text{--MDEA--H}_2\text{O}$ system. Good agreement between the results of the model and the result of NMR method (Jakobsen et al.,

2005) are obtained. In modeling the $\text{CO}_2\text{-MEA-H}_2\text{O}$ and the $\text{H}_2\text{S-MEA-H}_2\text{O}$ systems, to investigate the accuracy of the model, just the experimental data of (Fang-Yuan Jou, Mather, & Otto, 1995), (Jong Il Lee, Otto, & Mather, 1976) and (Lawson & Garst, 1976) are used to obtain the interaction

parameters then the data of the other references were used in order to predict the solubility of acid gases, so that, over 337 experimental data points were involved in calculations to correlate and predict the solubility of acid gases in aqueous MEA.

Table 11. Comparison of the Results of This Work and Those Obtained by Haghtalab and Mazloumi (2010) for the $\text{CO}_2\text{-MDEA-H}_2\text{O}$ and the $\text{H}_2\text{S-MDEA-H}_2\text{O}$ Systems

Author	np	This Work		Haghtalab and Mazloumi (2010)	
		*AAD%	**BIAS%	AAD%	BIAS%
<i>CO₂ – MDEA– H₂O</i>					
(Lemoine et al., 2000)	13	11.7	11.7	14.2	13.6
(Haji-Sulaiman et al., 1998)	42	13.9	9.5	15.0	12.4
(M. K. Park & Sandall, 2001)	30	12.6	5.3	20.7	10.8
(Sidi-Boumedine et al., 2004a)	77	11.7	-1.7	7.2	2.0
(Mamun et al., 2005)	34	7.7	-5.4	6.5	-0.9
(David M Austgen et al., 1991)	14	14.4	-4.3	15.4	-5.7
(Kuranov et al., 1996)	78	5.6	1.5	6.3	6.1
(Rho et al., 1997)	58	8.0	0.7	16.9	10.1
(Á. P.-S. Kamps et al., 2001)	28	10.4	-7.6	3.7	1.5
(Rogers et al., 1998)	34	14.6	14.6	21.7	0.0
(Macgregor & Mather, 1991)	5	16.8	5.1	17.2	12.2
<i>H₂S – MDEA– H₂O</i>					
(Lemoine et al., 2000)	27	13.2	13.2	26.8	28.1
(Sidi-Boumedine et al., 2004b)	25	9.5	3.6	8.0	1.6
(Kuranov et al., 1996)	71	2.4	2.2	1.4	0.8
(Á. P.-S. Kamps et al., 2001)	26	7.3	3.7	5.8	-1.2
(Rogers et al., 1998)	22	11.9	0.0	20.9	-18.0
(Macgregor & Mather, 1991)	18	10.5	0.0	21.6	-24.8
total	602	9.5	2.32	11.6	3.6

$$* \text{AAD\%} = (100 / np) \sum | (P_{\text{exp}} - P_{\text{cal}}) / P_{\text{exp}} |$$

$$** \text{BIAS\%} = (100 / np) \sum (P_{\text{exp}} - P_{\text{cal}}) / P_{\text{exp}}$$

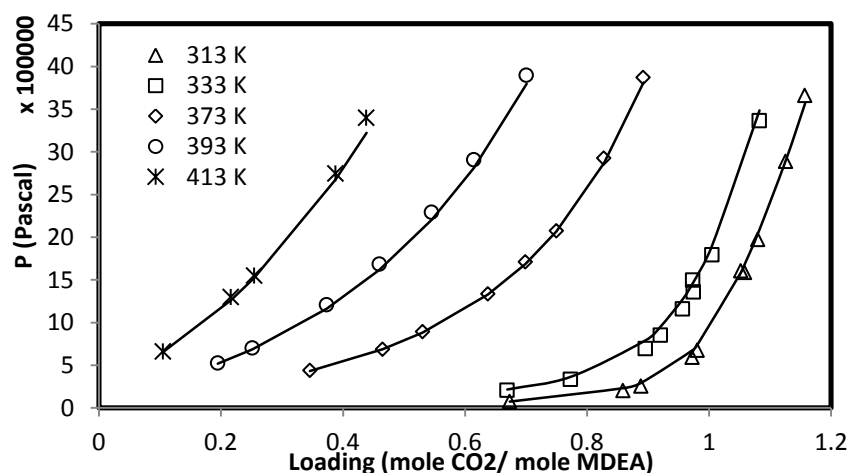


Figure 2. Comparison of Calculated and Experimental (Kuranov et al., 1996) Total Pressure of the $\text{CO}_2\text{-MDEA-H}_2\text{O}$ System in 32.2 wt% Alkanolamine at Various Temperatures.

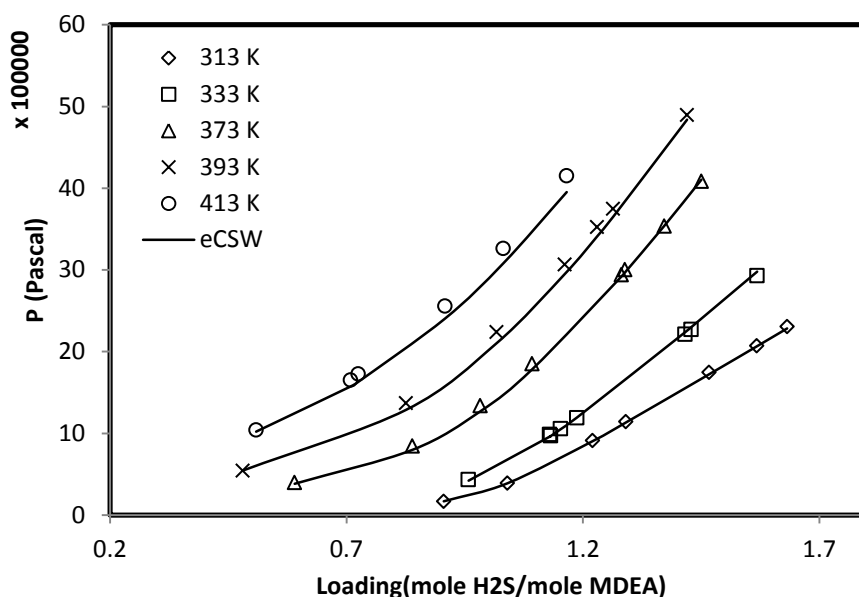


Figure 3. Comparison of Calculated and Experimental (Kuranov et al., 1996) Total Pressure of the H_2S -MDEA- H_2O System in 32.2 wt % Alkanolamine at Various Temperatures.

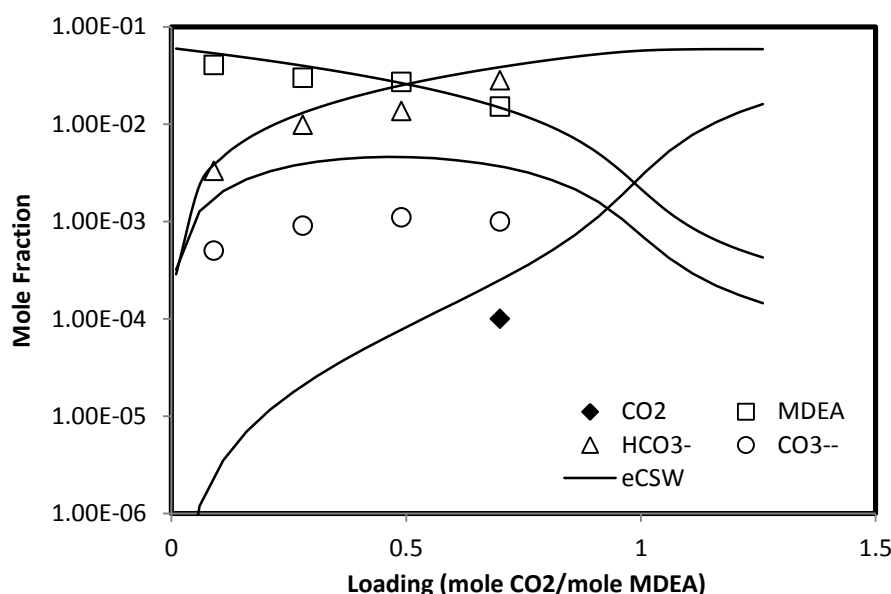


Figure 4. Comparison of Calculated Mole Fraction of Various Species with those Obtained by NMR Study (Jakobsen et al., 2005) for Solubility CO_2 in 23 wt % MDEA at 313 K.

Also, for modeling the CO_2 -DEA- H_2O and the H_2S -DEA- H_2O systems, this procedure is repeated and the data of (Jong Il Lee, Otto, & Mather, 1972) and (Lal, Otto, & Mather, 1985) for the solubility of CO_2 , and the data of (Jong Il Lee, Otto, & Mather, 1973a, 1973b) for solubility of H_2S , are selected to correlate, because the data of these references are in wide range of temperature, amine concentration, and acid gas loading. Then, other references are used to predict the solubility of acid gases in aqueous DEA. Also in these systems more than 670 experimental data points were used. The

results of correlation and prediction for system of these primary and secondary amines have been shown in table 12. As it is observed from this table, the errors are a little high. Generally, when the experimental data are in wide range of temperature, pressure and acid gas loading, the values of errors in modeling are not low. For example, (Y.-G. Li & Mather, 1997), have obtained the errors in range of 12 to 52 percents of absolute average deviation in correlating and predicting the solubility of acid gases in aqueous MDEA (Vallée et al., 1999) using the model of (Clegg & Pitzer, 1992). And also, in this work, no experimental data were removed from the database. In Figure 5, the comparison of the

calculated and experimental (Fang-Yuan Jou et al., 1995) partial pressure against acid gas loading for the CO_2 – MEA – H_2O system by 30 wt % of MEA at various temperatures have been presented. Similarly, the results of eCSW EoS for the solubility of H_2S in the aqueous MEA have been shown in Figure 6. Also, Figure 7 shows the prediction of the eCSW model for the CO_2 – MEA – H_2O system at various concentrations, temperature, and data sources (Bhairi, 1984; Lawson & Garst, 1976). As one can see the results of the present eEoS are in good agreement with experimental data. For the CO_2 – DEA – H_2O and the H_2S – DEA – H_2O

systems, the results of modeling of the solubility of acid gases in aqueous DEA have been presented in Figures 8 and 9. These figures show the comparison of calculated and experimental (Jong Il Lee et al., 1972, 1973b) partial pressure of CO_2 and H_2S in alkanolamine, respectively. Also, in Figure 10 the comparison of calculated mole fraction of various species with mole fraction obtained by NMR study (Bottinger, Maiwald, & Hasse, 2008) for CO_2 solubility in 30 wt % DEA at 313 K have been shown. As one can see from the figures, very good accuracy of the eEoS model is observed.

Table 12. Percent of Absolute Average Deviation in Predicting and Correlating the Bubble Pressure of the Solubility of Acid Gases in Aqueous MEA and DEA Solutions for Ternary Systems

Author	np	Corr.		Pred.	
		AAD%	BIAS%	AAD%	BIAS%
<i>CO₂ – MEA – H₂O</i>					
(Fang-Yuan Jou et al., 1995)	80	25.00	16.53		
(Bhairi, 1984)	60			17.94	-4.18
(Lawson & Garst, 1976)	13			13.34	-3.06
(David M Austgen et al., 1991)	8			16.51	7.52
(Mamun et al., 2005)	19			13.82	-6.30
(J.-Y. Park et al., 2003)	9			7.30	-2.75
(Jane & Li, 1997)	6			8.70	0.00
<i>H₂S – MEA – H₂O</i>					
(Jong Il Lee et al., 1976)	96	16.93	1.95		
(Lawson & Garst, 1976)	45	15.56	15.30		
(Bhairi, 1984)	18			14.72	-0.23
Total	337				
<i>CO₂ – DEA – H₂O</i>					
(Jong Il Lee et al., 1972)	104	17.85	-7.73		
(Lawson & Garst, 1976)	30			15.67	-9.34
(Bhairi, 1984)	25			19.85	-19.85
(Lal et al., 1985)	44	4.11	-2.28		
(Oyevaar et al., 1989)	14			14.48	1.57
(Dawodu & Meisen, 1994)	6			7.00	1.94
(Haji-Sulaiman et al., 1998)	45			23.11	2.30
(Sidi-Boumedine et al., 2004a)	24			17.32	-11.08
(Rogers et al., 1997)	14			14.02	8.47
<i>H₂S – DEA – H₂O</i>					
(Jong Il Lee et al., 1973a)	112	18.56	-10.90		
(Jong Il Lee et al., 1973b)	166	18.23	-1.40		
(Lawson & Garst, 1976)	89			20.04	-15.80
Total	673				

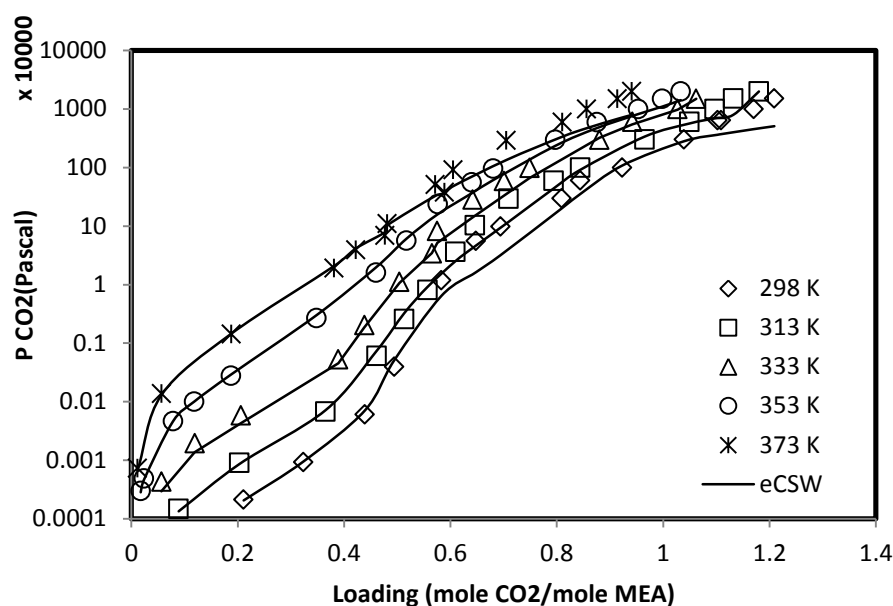


Figure 5. Comparison of Calculated and Experimental (Fang-Yuan Jou et al., 1995) Partial Pressure of the CO_2 -MEA- H_2O System in 30 wt % Alkanolamine at Various Temperatures.

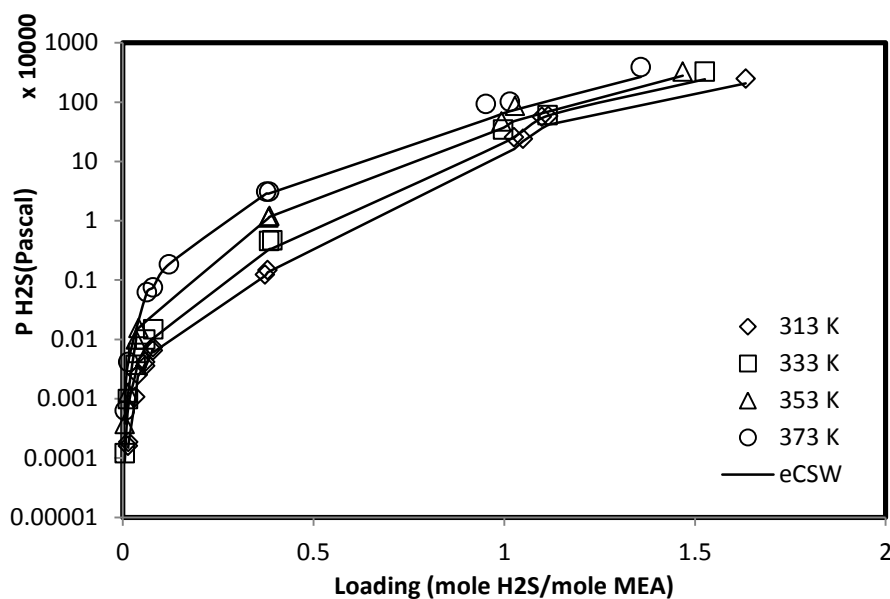


Figure 6. Comparison of Calculated and Experimental (Lawson & Garst, 1976) Partial Pressure of the H_2S -MEA- H_2O System in 15.2 wt % Alkanolamine at Various Temperatures.

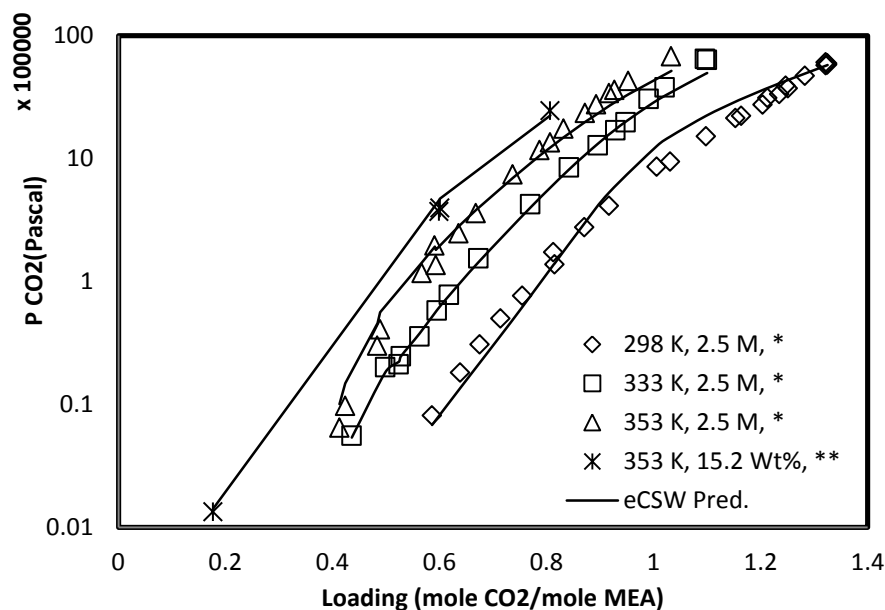


Figure 7. Comparison of Predicted and Experimental *(Bhairi, 1984; Lawson & Garst, 1976)** Partial Pressure of the $\text{CO}_2 - \text{MEA} - \text{H}_2\text{O}$ System in 2.5 M and 15.2 wt % Alkanolamine at Various Temperatures and Sources.

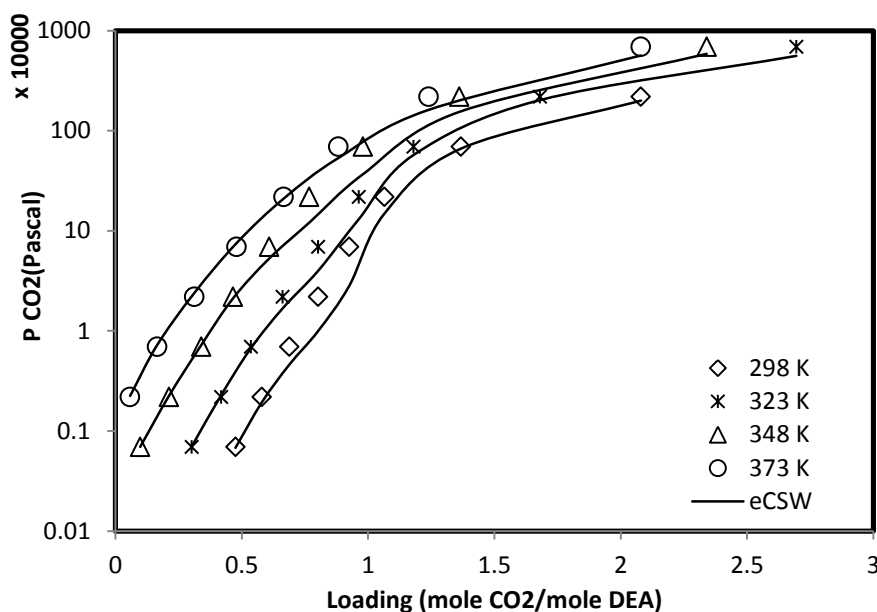


Figure 8. Comparison of Calculated and Experimental (Jong Il Lee et al., 1972) Partial Pressure of the $\text{CO}_2 - \text{DEA} - \text{H}_2\text{O}$ System in 0.5 M Alkanolamine at Various Temperatures.

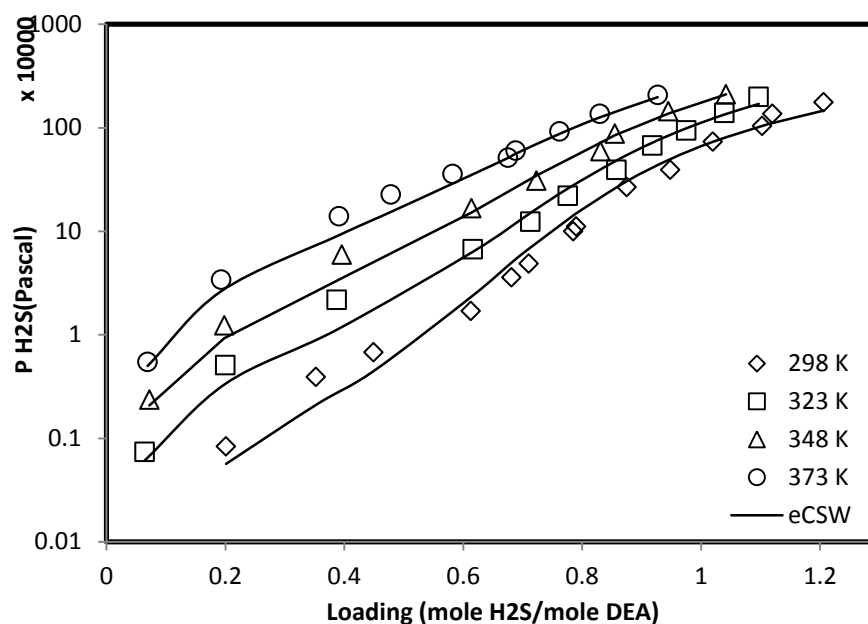


Figure 9. Comparison of Calculated and Experimental (Jong Il Lee et al., 1973a) Partial Pressure of the $H_2S-DEA-H_2O$ System in 3.5 M Alkanolamine at Various Temperatures.

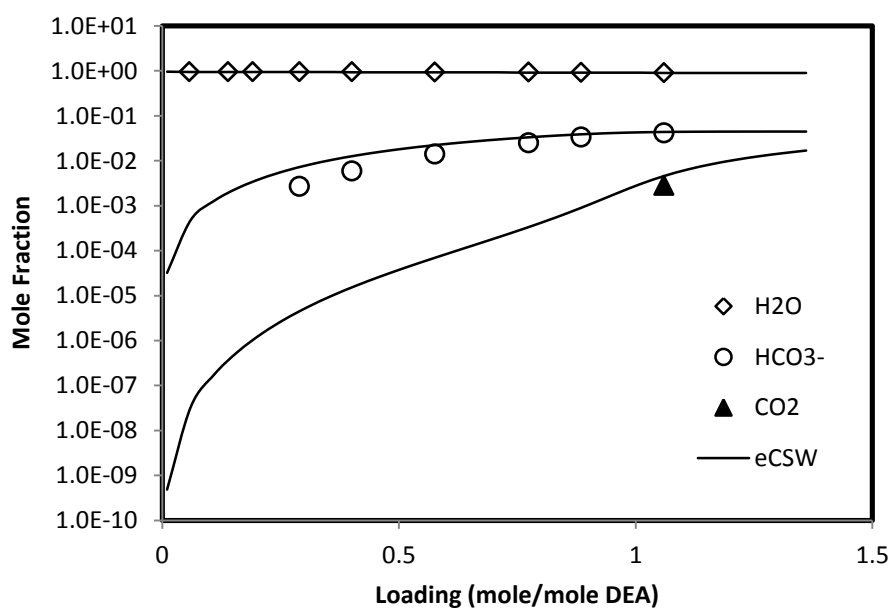


Figure 10. Comparison of Calculated Mole Fraction of Various Species with those Obtained by NMR Study (Bottinger et al., 2008) for Solubility CO_2 in 30 wt % DEA at 313 K.

For the solubility of CO_2 and H_2S in aqueous AMP, DIPA, PZ, TEA, and DGA solutions, the calculations are same as previous procedure. So that, the number of one and/or two references have been used to correlate, then the other references were used in order to predict the solubility of acid gases in alkanolamine solutions, except TEA and DGA,

that all of the experimental data of these systems were correlated. Table 13, shows the AAD% and BIAS% of the EoS model for the solubility of acid gases in aqueous AMP, DIPA, PZ, TEA, and DGA solutions. Also, in table 14 and 15, the ionic interaction parameters that were calculated by using eCSW, have been shown.

Table 13. Percent of Absolute Average Deviation in Predicting and Correlating the Bubble Pressure of the Solubility of Acid Gases in Aqueous *AMP*, *DIPA*, *PZ*, *TEA* and *DGA* Solutions for Ternary Systems

Author	np	Corr.		Pred.	
		AAD%	BIAS%	AAD%	BIAS%
<i>CO₂ – AMP – H₂O</i>					
(Tontiwachwuthikul et al., 1991)	40	15.42	3.09		
(Kundu et al., 2003)	51	17.00	7.10		
(Silkenbaumer et al., 1998)	66			24.56	8.73
(Jamal, 2002)	30			21.28	11.17
(Haji-Sulaiman & Aroua, 1996)	20			21.32	3.22
(Yang et al., 2010)	8			5.40	0.93
(Jane & Li, 1997)	8			5.14	0.99
(Roberts & Mather, 1988)	36			18.22	10.66
(Teng & Mather, 1990)	24			10.09	5.45
<i>H₂S – AMP – H₂O</i>					
(M.-H. Li & Chang, 1994)	41	8.97	-1.45	8.97	-1.45
(Jane & Li, 1997)	9			3.67	-0.75
(Roberts & Mather, 1988)	27			12.38	1.14
Total	360				
<i>CO₂ – DIPA – H₂O</i>					
(Isaacs et al., 1977)	45	23.95	-9.75		
<i>H₂S – DIPA – H₂O</i>					
(Isaacs et al., 1977)	26			10.27	4.60
(Mazloumi et al., 2012)	23	7.91	2.52		
(Uusi-Kyyny et al., 2013)	77			11.14	10.49
Total	171				
<i>CO₂ – PZ – H₂O</i>					
(A. P.-S. Kamps et al., 2003)	92	22.04	-1.12		
(P. W. Derks et al., 2005)	52			24.47	-22.43
(Ermatchkov et al., 2006)	33			21.35	-20.86
<i>H₂S – PZ – H₂O</i>					
(Xia et al., 2003)	82	9.08	2.66		
(Speyer & Maurer, 2011)	25			12.61	-11.36
Total	284				
<i>CO₂ – TEA – H₂O</i>					
(Cheng et al., 2010)	30	17.36	-11.47		
<i>H₂S – TEA – H₂O</i>					
(Atwood et al., 1957)	17	14.19	12.38		
Total	47				
<i>CO₂ – DGA – H₂O</i>					
(Martin et al., 1978)	46	12.25	10.78		
(Chen, 1991)	43	16.37	-0.13		
<i>H₂S – DGA – H₂O</i>					
(Martin et al., 1978)	36	11.52	7.23		
Total	125				

Table 14. Adjustable Binary Parameters Obtained by Correlation of the Bubble Pressure of the Ternary Aqueous Acid Gas-Alkanolamine Systems for *MDEA*, *MEA*, *DEA* and *AMP* Solutions

Parameters	<i>MDEA</i>		<i>MEA</i>		<i>DEA</i>		<i>AMP</i>	
	b_1	b_2	b_1	b_2	b_1	b_2	b_1	b_2
$k_{\text{CO}_2-\text{AMINEH}^+}$	0.7807	-172.00	0.3090	-0.11	0.3062	0.08	0.1625	-0.02
$k_{\text{HCO}_3^- - \text{AMINEH}^+}$	0.2113	-43.63	-0.0544	0.25	-0.1411	-0.06	0.2106	0.09
$k_{\text{CO}_3^{2-} - \text{AMINEH}^+}$	0.8811	-0.13	-0.4782	-0.23	-0.1592	-0.33	-0.1374	-0.8
$k_{\text{H}_2\text{O}-\text{AMINEH}^+}$	-0.1720	52.02	-0.0381	0.22	-0.0336	0.01	0.0328	0.11
$k_{\text{OH}^- - \text{AMINEH}^+}$	-0.0379	-0.01	0.1790	-0.28	0.1996	-0.04	-0.1163	-0.04
$k_{\text{H}_2\text{S}-\text{AMINEH}^+}$	-0.3212	103.91	-0.1219	0.06	0.1364	0.21	0.1445	0.06
$k_{\text{HS}^- - \text{AMINEH}^+}$	0.1467	-22.16	0.3054	0.29	0.0049	0.05	-0.4252	0.06
$k_{\text{S}^{2-} - \text{AMINEH}^+}$	-0.5603	1.85	-0.2163	0.08	-0.0779	0.01	-0.0584	-0.00
$k_{\text{AMINE}-\text{AMINEH}^+}$	0.1720	-52.02	-0.0613	0.15	-0.2167	0.09	-0.1200	-0.01
$k_{\text{AMINECOO}^- - \text{AMINEH}^+}$	--	--	-0.3336	0.14	-0.0870	0.00	0.0528	0.01

Table 15. Adjustable Binary Parameters Obtained by Correlation of the Bubble Pressure of the Ternary Aqueous Acid Gas-Alkanolamine Systems for *DIPA*, *TEA*, *DGA* and *PZ* Solutions

Parameters	<i>DIPA</i>		<i>TEA</i>		<i>DGA</i>		<i>PZ</i>	
	b_1	b_2	b_1	b_2	b_1	b_2	b_1	b_2
$k_{\text{CO}_2-\text{AMINEH}^+}$	0.0132	0.05	0.8811	-0.13	-0.0226	-0.01	0.1566	0.07
$k_{\text{HCO}_3^- - \text{AMINEH}^+}$	0.0171	0.04	-0.0379	-0.01	-0.1070	-0.33	-0.2789	-0.10
$k_{\text{CO}_3^{2-} - \text{AMINEH}^+}$	0.0231	0.03	-0.5603	1.78	0.0740	0.30	0.0813	-0.02
$k_{\text{H}_2\text{O}-\text{AMINEH}^+}$	-0.0084	0.01	0.6494	53.83	-0.1566	0.09	0.0256	0.03
$k_{\text{OH}^- - \text{AMINEH}^+}$	0.0422	0.01	-0.1683	16.36	0.1741	-0.16	-0.0229	-0.03
$k_{\text{H}_2\text{S}-\text{AMINEH}^+}$	-0.0510	0.04	-0.6144	-7.40	0.0689	-0.10	0.0140	-0.03
$k_{\text{HS}^- - \text{AMINEH}^+}$	-0.1473	0.17	0.8573	13.91	0.9501	0.02	0.1900	0.07
$k_{\text{S}^{2-} - \text{AMINEH}^+}$	0.0264	-0.31	0.2104	-0.59	0.0448	0.03	-0.0601	0.37
$k_{\text{AMINE}-\text{AMINEH}^+}$	-0.0160	-0.03	-0.3084	0.35	0.2014	-0.55	0.1853	-0.22
$k_{\text{AMINECOO}^- - \text{AMINEH}^+}$	0.0267	0.06	--	--	0.9353	0.07	0.0008	0.07

In Figure 11, using the ratio of calculated and experimental pressure, the deviation versus the CO_2 loading for the CO_2 –*AMP*– H_2O system was observed. As one can see, the most of the points are below the horizontal line. It means the results of the eCSW EoS model are under correlated. Also, Figure 12 shows the ratio of calculated and experimental partial pressure of CO_2 against the temperature for CO_2 –*AMP*– H_2O system. Also in this figure,

an under-correlation is observed in the most data points.

Figure 13 shows the predicted of partial pressure of H_2S by eCSW EoS in aqueous *DIPA* solution against temperature in various acid gas loading. The predicted values are in good agreement with experiment (Isaacs, Otto, & Mather, 1977), but a little deviation is evident in low temperatures. A comparison between the experimental (Ermatchkov,

Kamps, Speyer, & Maurer, 2006) and calculated partial pressure of H_2S in the $H_2S-PZ-H_2O$ system by 14.57 wt % of PZ at various temperatures is shown in Figure 14. It

can be seen that, except high acid gas loadings and temperatures, the results are in very good agreement with experiment.

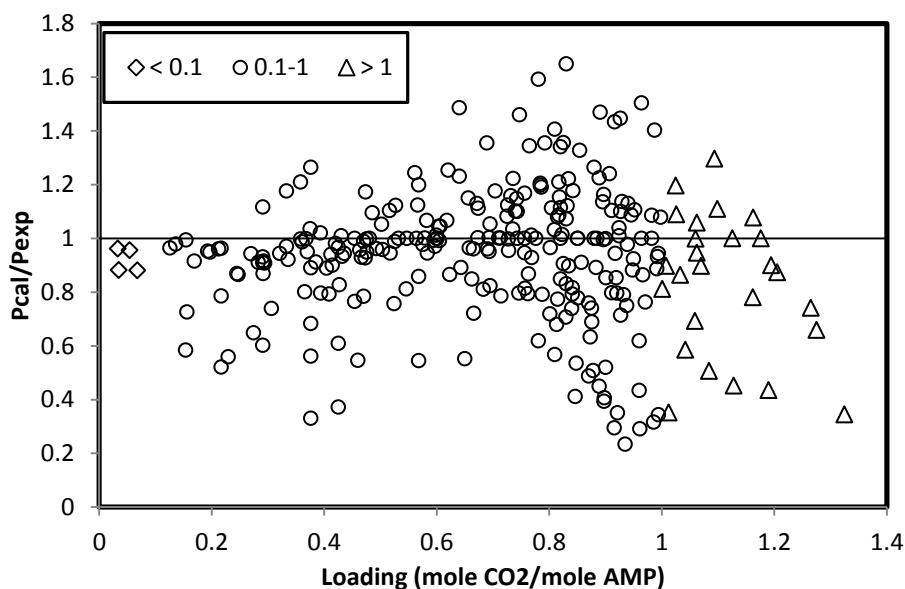


Figure 11. Ratio of Calculated Pressure to the Experimental Pressure for each Data point Against Loading of CO_2 in the $CO_2-AMP-H_2O$ Ternary System.

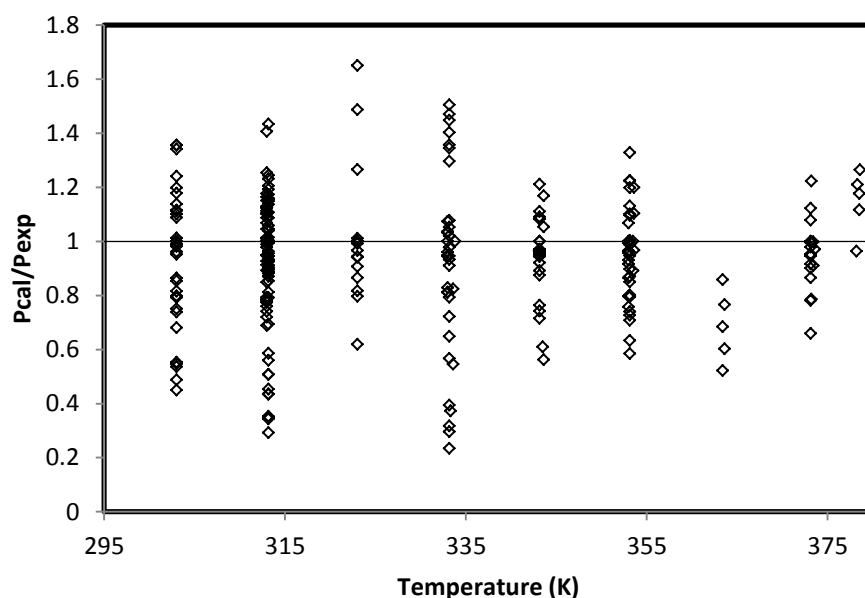


Figure 12. Ratio of Calculated Pressure to the Experimental Pressure at Different Temperatures in the $CO_2-AMP-H_2O$ Ternary System.

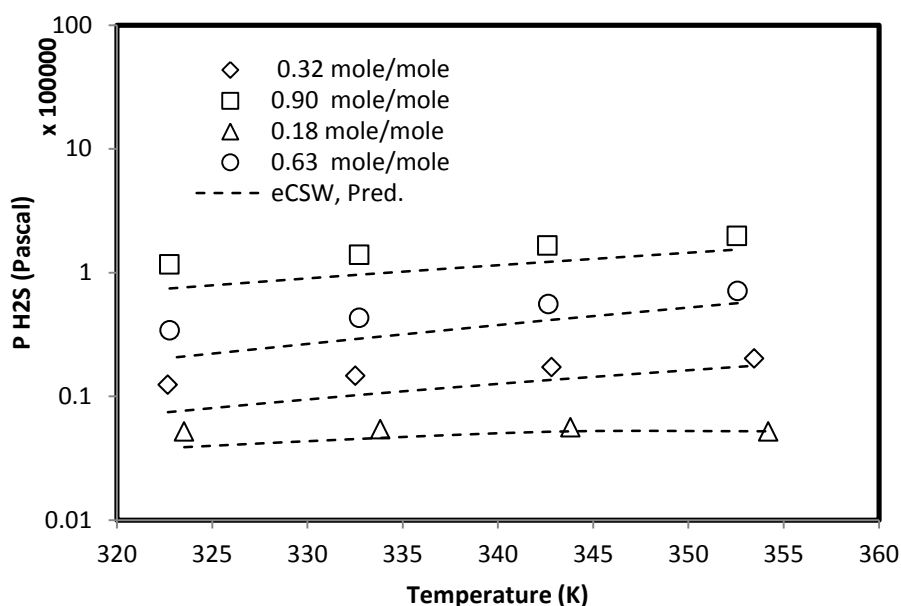


Figure 13. Comparison of Predicted and Experimental (Isaacs et al., 1977) Partial Pressure of the H_2S –DIPA– H_2O System in 2.5 M Alkanolamine Against Temperature at Various H_2S Loading.

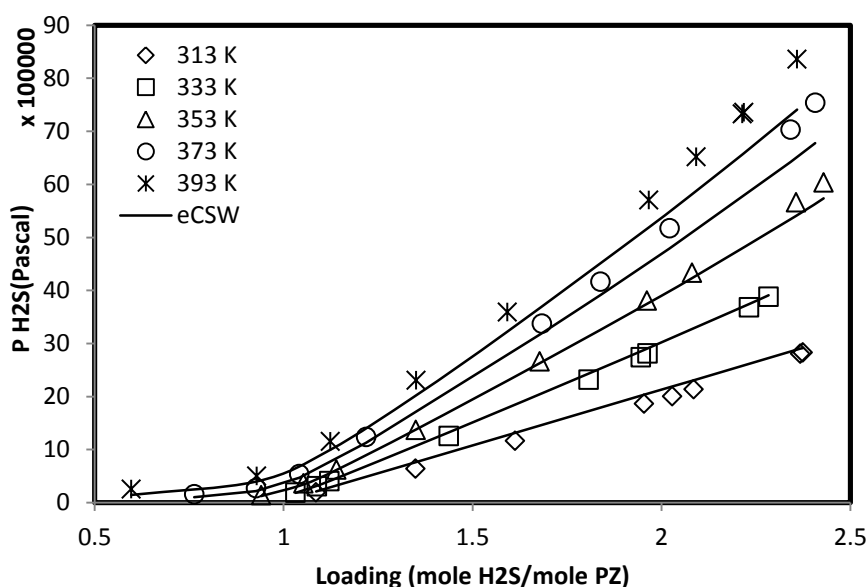


Figure 14. Comparison of Calculated and Experimental (Ermatchkov et al., 2006) Partial Pressure of the H_2S –PZ– H_2O System in 14.57 wt % Alkanolamine at Various Temperatures.

3.5. The Quaternary Systems

In order to show the predictability of the eCSW EoS model for the quaternary systems, without adjusting any new interaction parameters, the solubility of mixed acid gases in aqueous MEA, DEA, MDEA, TEA and AMP solutions is computed. As shown in table 16, 370 number of experimental data points are used in various amine concentrations, acid gas loadings, and partial pressures for modeling of quaternary

systems by present EoS model. Also, in table 17, the AADs and BIASs of modeling are observed. These results seem to be acceptable. In Figures 15, 16 and 17, the predicted pressure against experimental pressure are plotted in various temperatures and amine concentrations, respectively, for the quaternary CO_2 – H_2S –MDEA– H_2O , CO_2 – H_2S –DEA– H_2O and CO_2 – H_2S –AMP– H_2O systems. It can be observed that the results of model are in line with the experiments.

Table 16. Specifications of the Experimental Data Sources Used for the Solubility of Acid Gases in Aqueous Alkanolamine Solutions for Quaternary Systems

System	T(K)	Amine (Wt%)	Loading (mole/mole)		Pressure (kPa)		np
			CO ₂	H ₂ S	CO ₂	H ₂ S	
CO ₂ – H ₂ S – MEA – H ₂ O							
(J. I. Lee, Otto, & Mather, 1974)	313	30.43	0.116-1	0.0-0.3	0.068	2.068	34
CO ₂ – H ₂ S – DEA – H ₂ O							
(J. I. Lee et al., 1974)	323	20.67	0.04-1.22	0.012-1.0	0.21-5764	0.8-1505	58
(Lawson & Garst, 1976)	310-394	25	0.07-0.93	0.0056-1.0	1.4-2293	0.8-2199	84
(Rogers et al., 1997)	322	20	0.006-0.2	0.001-0.56	0.0003-0.5	0.0001-0.5	25
CO ₂ – H ₂ S – MDEA – H ₂ O							
(Fang-Yuan Jou, Carroll, Mather, & Otto, 1993)	373, 313	35	0.0-0.788	0.0-0.88	0.005-529	0.032-196	106
(Rogers et al., 1998)	313, 323	23, 50	0.0-0.102	0.0-0.20	0.004-1.67	0.002-2.65	22
CO ₂ – H ₂ S – TEA – H ₂ O							
(Fang-Yuan Jou, Otto, & Mather, 1996)	323	28.63	0.07-1.37	0.001-1.0	0.40-5650	0.53-1050	15
CO ₂ – H ₂ S – AMP – H ₂ O							
(Jane & Li, 1997)	313, 353	30	0.11-0.56	0.14-0.55	1.17-8.38	2.240-74.5	30
Total							372

Table 17. Percent of Absolute Average Deviation in Predicting of the Bubble Pressure of the Solubility of Mixed Acid Gases in Aqueous *MEA*, *DEA*, *MDEA*, *TEA* and *AMP* Solutions for Quaternary Systems.

System	np	AAD%	BIAS%
CO₂ – H₂S – MEA – H₂O			
(J. I. Lee et al., 1974)	34	26.17	11.48
CO₂ – H₂S – DEA – H₂O			
(J. I. Lee et al., 1974)	58	26.74	-25.63
(Lawson & Garst, 1976)	84	31.11	24.64
(Rogers et al., 1997)	25	7.63	7.54
CO₂ – H₂S – MDEA – H₂O			
(Fang-Yuan Jou et al., 1993)	106	26.80	19.49
(Rogers et al., 1998)	22	12.20	-12.20
CO₂ – H₂S – TEA – H₂O			
(Fang-Yuan Jou et al., 1996)	15	23.21	-12.79
CO₂ – H₂S – AMP – H₂O			
(Jane & Li, 1997)	30	27.00	15.08
Total	372		

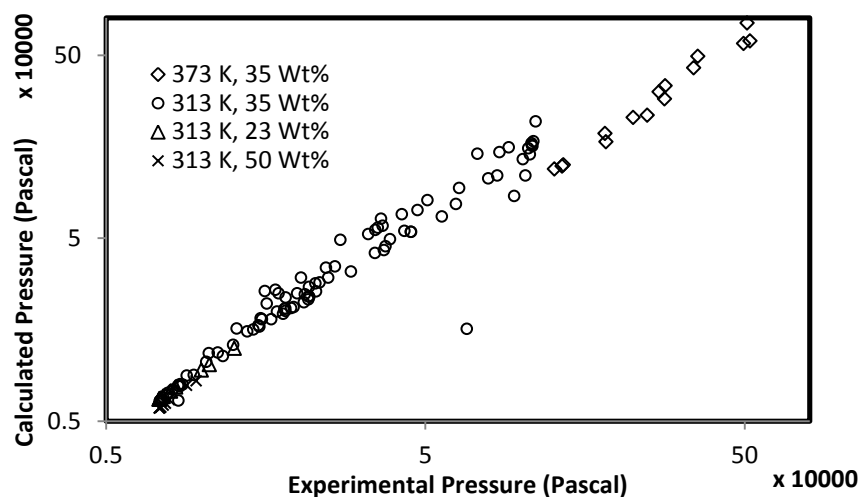


Figure 15. Comparison of the Predicted Total Pressure by eCSW and the Experimental Data for the $\text{CO}_2 - \text{H}_2\text{S} - \text{MDEA} - \text{H}_2\text{O}$ Quaternary System.

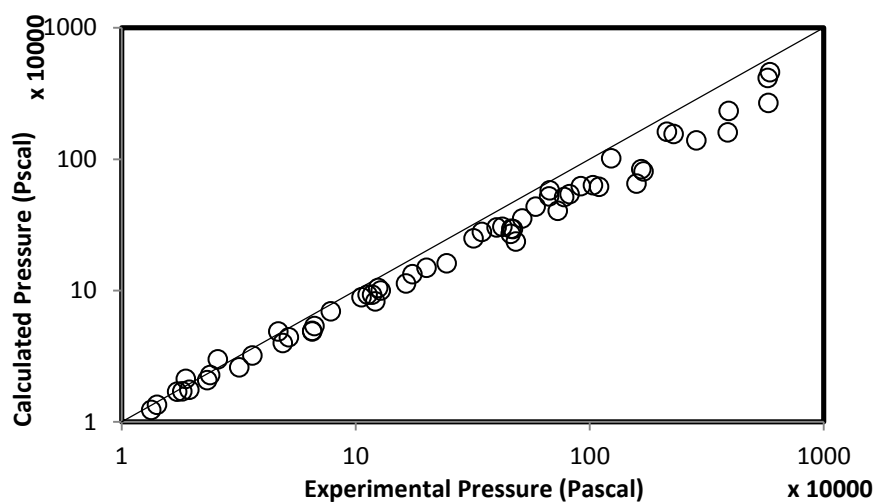


Figure 16. Comparison of the Predicted Total Pressure by eCSW and the Experimental Data for the $\text{CO}_2 - \text{H}_2\text{S} - \text{DEA} - \text{H}_2\text{O}$ Quaternary System.

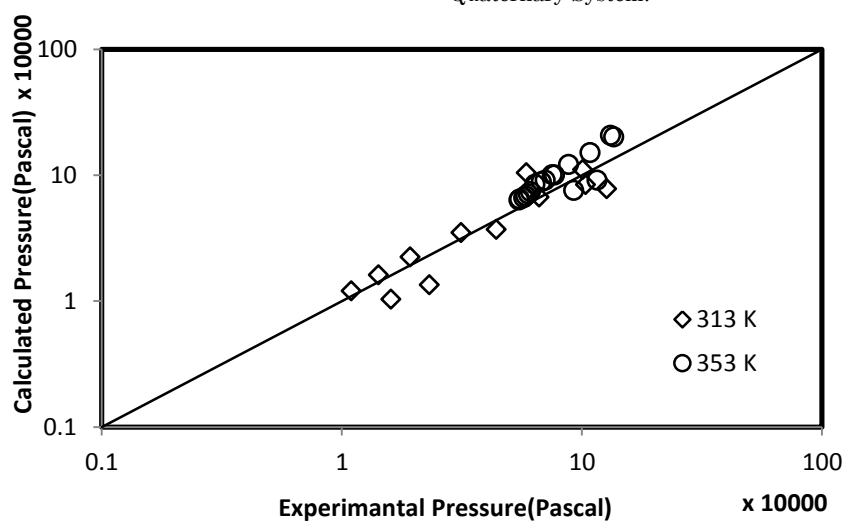


Figure 17. Comparison of the Predicted Total Pressure by eCSW and the Experimental Data for the $\text{CO}_2 - \text{H}_2\text{S} - \text{AMP} - \text{H}_2\text{O}$ Quaternary System.

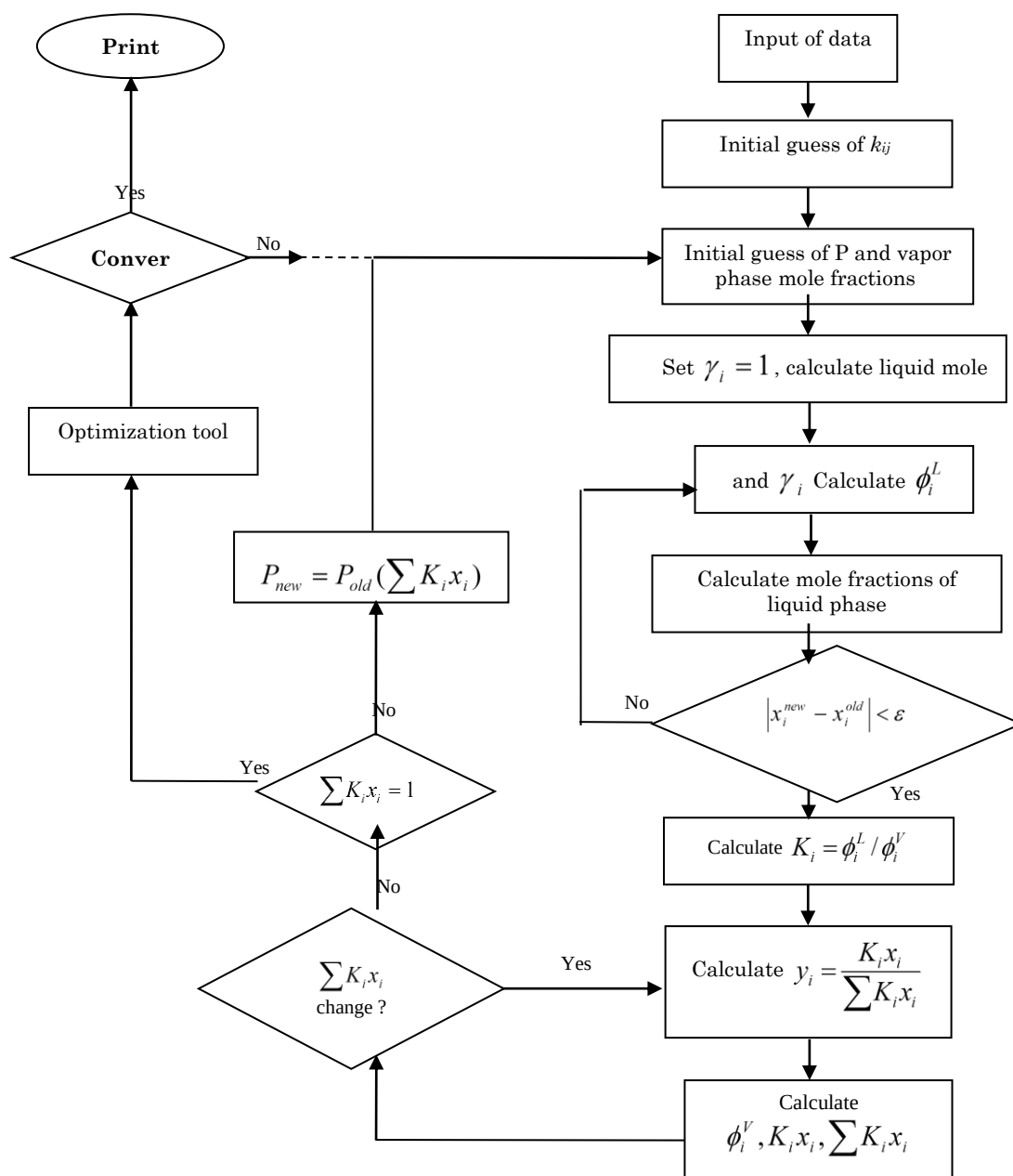


Figure B.1. Flowchart of Simultaneously Calculation of Chemical and Physical Equilibrium.

4. Conclusions

In this work, over 3000 experimental data points were used in order to correlate and predict the solubility of CO_2 and H_2S in alkanolamine solutions by eCSW EoS model. A comparison between this work and the work of (Ali Haghtalab & Mazloumi, 2010) was carried out. The decreases of 2.1 and 1.28 percents, respectively, for AAD% and BIAS% were achieved in modeling the CO_2 -MDEA- H_2O and H_2S -MDEA- H_2O systems. Then, the eEoS systematically was applied to describe the solubility of acid gases in various alkanolamine solutions, i.e. MDEA, MEA, DEA, AMP, DIPA,

TEA, DGA and PZ. The results of the eCSW were in good agreements with the experiment. After that, to investigate the accuracy of the modeling, the simultaneous solubility of mixed CO_2 and H_2S in aqueous MEA, DEA, MDEA, TEA and AMP solutions were predicted, and the acceptable results were achieved for the quaternary systems. The results show that eCSW EoS can be used successfully for correlating and predicting the solubility of CO_2 and H_2S in various alkanolamines in wide range of temperature, acid gas loading and pressure.

Appendix A. The Electrolyte Cubic Square-Well (eCSW) EoS.

The basic equation of the model is based on a Helmholtz free energy expression. This equation can be written by three contributions as:

$$a^{res}(T, \nu, x_i) = a - a^{id} = a_{CSW} + a_{MSA} + a_{Born} \quad (A.1)$$

Where subscript "CSW" and "MSA" stand for the cubic square well EoS and mean spherical approximation theory, respectively. The Born equation is used for discharging and charging processes as (Ali Haghtalab & Seyed Hossein Mazloumi, 2009):

$$a_{Born} = -\frac{N_A e^2}{4\pi\epsilon_0} \left(1 - \frac{1}{D}\right) \sum_{ions} \frac{x_i Z_i^2}{\sigma_i} \quad (A.2)$$

where e is the unit of elementary charge, ϵ_0 is permittivity of the free space, D is the dielectric constant, Z is the charge number of ions and N_A is Avogadro's number. The pressure and chemical potential equations of the Born equation are given as:

$$P_{Born} = 0 \quad (A.3)$$

$$\frac{\mu_{i,Born}}{RT} = \frac{e^2 N_A}{4\pi\epsilon_0 RT} \left(-\frac{1}{D^2} \frac{\partial D}{\partial n_i} \sum_{ions} \frac{n_i Z_i^2}{\sigma_i} - \frac{Z_i^2}{\sigma_i} \left(1 - \frac{1}{D}\right) \right) \quad (A.4)$$

where $\partial D / \partial n_i$ and D are calculated as (Ali Haghtalab & Mazloumi, 2010):

$$\left(\frac{\partial D}{\partial n_i} \right)_{T, \nu, n_{jsi}} = \frac{1}{n_i} \frac{D_s - D}{\sum_s x_s} \quad i = s = H_2O \& AMINE \quad (A.5)$$

$$D = \frac{\sum_s x_s D_s}{\sum_s x_s} \quad (A.6)$$

where subscript s denotes pure solvent. It should be pointed out that for the other species, i.e., acid gases and ions, $\partial D / \partial n_i = 0$. The dielectric constants for pure solvents are given in table 1. For the long range contribution of the ions, the explicit version of MSA is applied as (Ali Haghtalab & Seyed Hossein Mazloumi, 2009):

$$a_{MSA} = -\frac{2\Gamma^3 RT \nu}{3\pi N_A} \left(1 + \frac{3}{2} \sigma \Gamma\right) \quad (A.7)$$

where Γ is the MSA screening parameter are computed as:

$$\Gamma = \frac{1}{2\sigma} \left[\sqrt{1 + 2\sigma\kappa} - 1 \right] \quad (A.8)$$

$$\kappa^2 = \frac{e^2 N_A^2}{D \epsilon_0 RT \nu} \sum_{ions} x_i Z_i^2 \quad (A.9)$$

In the above relations, κ is the Debye screening length, σ is the average diameter of ions that is computed using linear mixing rule as:

$$\sigma = \frac{\sum_{ions} x_i \sigma_i}{\sum_{ions} x_i} \quad (A.10)$$

The pressure and chemical potential equations of the MSA contribution are expressed as:

$$P_{MSA} = \frac{2\Gamma^3 RT}{3\pi N_A} \left(1 + \frac{3}{2} \sigma \Gamma\right) - \frac{RT \kappa^2}{4\pi N_A} \frac{\Gamma}{1 + \Gamma} \quad (A.11)$$

$$\frac{\mu_{i,MSA}}{RT} = \frac{e^2 N_A}{4\pi D \epsilon_0 RT} \frac{\Gamma}{1 + \sigma \Gamma} \left(-Z_i^2 + \frac{1}{D} \frac{\partial D}{\partial n_i} \sum_{ions} n_i Z_i^2 \right) \quad (A.12)$$

The contribution of the molar Helmholtz energy from the square well potential, following (A. Haghtalab & S. H. Mazloumi, 2009), is presented as:

$$a_{CSW} = RT \ln \left(\frac{\nu}{\nu - 4\tau \nu_0} \right) - \frac{zRT}{2} \ln \left(\frac{m \nu + \nu_0 w}{m \nu + \nu_0 (1 - m)} \right) \quad (A.13)$$

The first term of Eq. (A.13) represents the Van der Waals repulsive force and the second term denotes the attractive force, base on square well potential. T is absolute temperature, ν is molar volume and τ is a constant value. The following mixing rules are used to generalize calculations for mixture as:

$$m = \sum_i \sum_j x_i x_j m_{ij} \quad (A.14)$$

$$w = \sum_i \sum_j x_i x_j w_{ij} = \sum_i \sum_j x_i x_j \left(\exp \left(\frac{\epsilon_{ij}}{kT} \right) - m_{ij} \right) \quad (A.15)$$

$$\nu_0 = \sum_i x_i \nu_{0i} \quad (A.16)$$

$$z = \sum_i x_i z_i \quad (\text{A.17})$$

$$m_{ij} = \frac{4\sqrt{2}\pi\lambda_{ij}^3 - 3}{4\sqrt{2}\pi(\lambda_{ij}^3 - 1)} \quad (\text{A.18})$$

$$\nu_{0i} = \frac{N_A \sigma_i^3}{\sqrt{2}} \quad (\text{A.19})$$

$$z_i = \frac{4\sqrt{2}\pi}{3} \lambda_{ii}^3 - 1 \quad (\text{A.20})$$

also the combining rules as:

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} (1 - k_{ij}) \quad (\text{A.21})$$

$$\lambda_{ij} = \frac{\sigma_i \lambda_i + \sigma_j \lambda_j}{\sigma_i + \sigma_j} \quad (\text{A.22})$$

where ε is the CSW potential depth, σ is the diameter of the species, λ is the potential range, and the coupling parameter, $k_{ij} = k_{ji}$ is the binary interactions parameter. In above equations, the variable z is maximum attainable coordination number, m is the orientational parameter and ν_0 is the closed packed volume and the note is that the summations is over all components, i.e. ions, solvents, and acid gases.

The pressure and chemical potential equations of the CSW EoS were illustrated as:

$$P_{CSW} = \frac{RT}{\nu - 4\tau\nu_0} + \frac{zRT}{2} \frac{(1-m-w)m\nu_0}{(m\nu + \nu_0 w)(m\nu + \nu_0(1-m))} \quad (\text{A.23})$$

$$\frac{\mu_{i,CSW}}{RT} = \ln\left(\frac{\nu}{\nu - 4\tau\nu_0}\right) + \frac{4\tau\nu_{0i}}{\nu - 4\tau\nu_0} - \frac{z_i}{2} \ln\left(\frac{m\nu + \nu_0 w}{m\nu + \nu_0(1-m)}\right) - \frac{z}{2} \left(\frac{2\nu \sum_j x_j m_{ij} + w\nu_{0i} + 2\nu_0 \sum_j x_j w_{ij}}{m\nu + \nu_0 w} - \frac{2(\nu - \nu_0) \sum_j x_j m_{ij} + (1-m)\nu_{0i} + 2\nu_0}{m\nu + \nu_0(1-m)} \right) \quad (\text{A.24})$$

So, having the chemical potential express, the fugacity coefficient for each component in a mixture is expressed as:

$$\varphi_i = \frac{RT}{P\nu} \exp\left(\frac{\mu_i^{res}}{RT}\right) = \frac{RT}{P\nu} \exp\left(\frac{\mu_{i,CSW}}{RT} + \frac{\mu_{i,MSA}}{RT} + \frac{\mu_{i,Born}}{RT}\right) \quad (\text{A.25})$$

Appendix B.

To do the calculations of Vapor-Liquid Equilibria (VLE) of acid gases-alkanolamine-water systems, simultaneous calculations of physical and chemical equilibrium are required. Fig. B.1 shows the flowchart for such calculations.

Nomenclature

A	Coefficient in Eq. (34)
a	Molar Helmholtz free energy ($Jmol^{-1}$)
B	Coefficient in Eq. (34)
b_i	Coefficients in Eq. (44)
C	Coefficient in Eq. (34)
D	Coefficient in Eq. (34) and dielectric constant of solution
D_s	Dielectric constant of solvent
d_i	Coefficient in Eq. (7)
e	Electronic charge ($1.60219 \times 10^{-19} C$)
K	Equilibrium constant
k	Boltzmann's constant ($1.38066 \times 10^{-23} JK^{-1}$)
k_{ij}	Coupling interaction parameter between species i and j
m	Orientational parameters defined in Eq. (14)
n	Number of mole
np	Number of data points
N_A	Avogadro's number ($6.02214 \times 10^{23} mol^{-1}$)
P	Pressure (Pascal)
R	Gas constant ($8.314 Jmol^{-1}K^{-1}$)
T	Temperature (K)
ν	Molar volume ($m^3 mol^{-1}$)
νdW	Van der Waals
ν_0	Close-packed volume ($m^3 mol^{-1}$) defined in Eq. (14)
x_i	Mole fraction of component i
z	Maximum coordination defined in Eq. (14)
Z_i	Charge number of ionic species i
w	A function of temperature defined in Eq. (14)
Greek Letters	
Γ	MSA screening parameters (m^{-1})
γ	Activity coefficient
λ	Square-well potential parameter

ε	Square-well potential depth (J)
ε_0	Vacuum permittivity ($8.85419 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$)
σ	Size parameter (m)
ϕ	Fugacity coefficient
κ	Debye screening length (m^{-1})
τ	Constant (0.7405)
ν	Stoichiometric number

Subscripts

<i>Born</i>	Born contribution
<i>CSW</i>	Cubic square-well
<i>cal</i>	Calculated properties
<i>exp</i>	Experimental properties
<i>i</i>	Component <i>i</i>
<i>ij</i>	Binary pair of <i>i</i> and <i>j</i>
<i>j</i>	Component <i>j</i>
<i>MSA</i>	Mean Spherical Approximation theory
<i>s</i>	Solvent

Superscripts

*	Unsymmetrical normalization
0	Pure state
∞	Infinite dilution

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