

Research Article

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Experimental Measurements and Thermodynamic Modelling of Carbon Dioxide Capture with use of 2-(Ethylamino) Ethanol

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Abstract

Carbon dioxide solubility was studied in 2.5 mass % and 5 mass % aqueous 2 (Ethylamino)ethanol (EAE; CAS 110-73-6) solution, an interesting secondary amine prepared mainly from renewable resources, at high loading rates, at three temperature ranges (293.00K, 313.15 K, 333.15 K), and in pressure range from 289 to 1011 kPa. In addition to that, heat capacity (cp) was measured of examined solution, allowing determination of temperature dependent coefficients of ideal gas heat capacity equation. Afterwards, the electrolyte Non Random Two-Liquid model's parameters were determined to represent the thermodynamic behaviour of the CO₂ – EAE – H₂O system with use of ASPEN® Plus V8.0 simulation software, indicating a good correlation between experimental and simulation results. As a consequence, model based calculation of the carbon dioxide capture with use of 2-(Ethylamino) ethanol is possible.

Keywords: Electrolyte NRTL model; 2-(Ethylamino) ethanol; Carbon dioxide capture; Biogas upgrading technology; Biomethane; Carbon capture and Storage

Introduction

Biogas produced through anaerobic digestion of organic wastes is already widely applicable process, which is often utilized in combined heat and power units (CHP). However, biogas can also be upgraded, which means removal of CO₂ to fulfil requirements as a vehicle fuel, or feeding it to the public natural gas grid. It is achieved with different techniques like pressure swing adsorption, water scrubbing or amine washing are applied to remove carbon dioxide, and allow maximal methane slippage [1].

The main goal of this research was preparation of the model, thus determination of binary interaction parameters, which can be applied for upgrading existing biogas power plants to biomethane plants. At such plants prior to biogas combustion at CHP unit H₂S is removed due to corrosion danger [1,2], therefore it was decided to concentrate only on CO₂ removal. Since amine scrubbing is the most technically and commercially mature method, which can be easily retrofitted to an existing plant [3], and according to Rochelle [4] in 2030 it probably will be the dominant method applied for coal-fired power plants, amine scrubbing was selected for this research. 2-(Ethylamino) ethanol (EAE) is a linear secondary amine which is linked to an ethyl group, was decided to be evaluated in this research. Unlike monoethanolamine (MEA), EAE has a small corrosion rate, even at higher concentrations. In addition, it requires less energy for regeneration, and the absorption rate is higher due to creation of moderate stability carbamate [5-8]. An additional advantage is that, produced from agriculture products or residues ethanol is used to produce ethylamine and ethylene oxide. Both those chemicals react to form EAE [9]. Moreover, methyldiethanolamine (MDEA) is often applied during amine washing to ensure H₂S removal [2], however its rate constant of second-order reaction is lower than for EAE [8], and existing biogas power plants already removed H₂S prior to combustion at CHP unit [1,2]. 2-(Ethylamino)ethanol has been already proved as an absorbent for CO₂ capture [9], and also as an activator in aqueous N,N-diethylethanolamine (DEEA) solutions [10]. However, there is still little experimental data on CO₂ capture with EAE at high loading rates (mol CO₂ mol EAE⁻¹ > 1), and while the focus was rather on kinetics of reaction [8-12], no publication on thermodynamic modelling representing vapour-liquid equilibrium in the CO₂ – EAE –

H₂O system was found. Therefore in this research the Electrolyte Non Random Two-Liquid (eNRTL) model was applied for modelling the EAE's performance, since it has been widely applied for other amines like MEA [13], MEA and DEA [14], DGA [15], DGA and MDEA [16].

Summarizing, the main intention of this article is evaluation of the 2-(Ethylamino) ethanol for upgrading biogas, and preparation of the eNRTL model parameter, in order to promote model calculation of carbon capture with EAE. Moreover, those parameters are essential for the development of efficient industry upgrading installations.

Materials and Methods

Experimental

Materials and solutions

All chemicals used during this research were of analytical reagent grade, and employed without further purification. CO₂ was acquired from Linde AG (purity 99,5 volume%), and 2-(Ethylamino)ethanol (EAE; CAS: 110-73-6) was acquired from Sigma-Aldrich Co. LLC. (purity of ≥98 volume%). In order to ensure excellent water quality necessary for HPLC pump, Milli-Q water was used, due to its high degree of de-ionizing and purity. It was prepared by use of Milli-Q Biocel unit (®EMD Millipore Corporation).

Before each experiment it was crucial to guarantee that water is not containing CO₂, with the purpose of ensuring that solubility measurements are accurate. Therefore, prior to each experiment vacuum was applied to Duran bottle, resistant to under- and over-pressure, filled with Milli-Q water. Afterwards aqueous alkanolamine

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solution was prepared gravimetrically. Subsequently prepared solution was purged with nitrogen, acquired from Linde AG (purity 99,999 volume%), before the final stage of placing it in ultrasonic bath (Branson 2210) for one hour.

Apparatus: In order to measure CO₂ solubility in aqueous alkanolamine solutions an experimental apparatus was developed, based on modified approach of Cadours et al. [17] The unit consists of two reactors acquired from Parr Instrument Company (4560 Pressure Reaction Apparatus; volume of 0.45 dm³; maximum working pressure of 20000 kPa; operating temperature from 263.15 K to 623.15 K) directly connected to each other with high pressure stainless steel capillary with double-sided conical bolt connection (A506HC; Hose Assembly 6FT T316), as presented on Figure 1.

The second reactor is equipped with a stirrer (A1120HC6 Parr Magnetic Drives; Turbine Type Impeller) controlled by Parr 4875 Power Controller. Gas bottles located in gas safety cabinet (Asecos, FWF 90) are connected to first reactor, also with use of Parr's high pressure capillaries (A495HC, Hose Assembly 6FT Nylon). Both reactors were heated up with use of Lauda water bath (Ecoline Staredition 006), and the temperature inside each reactor was measured with use of Parr's thermocouples (A472E2; Thermocouple 9-1/2, T316 stainless steel, Type J). Due to the measurement procedure (described in chapter 2.1.3) reactors were equipped with PR-33X pressure sensors, both acquired from Keller Druckmesstechnik, but with different pressure ranges: Keller PR-33X 0-1000 kPa (accuracy ±0.1% of full scale) and Keller PR-33X 0-3000 kPa (accuracy ±0.1% of full scale). Both sensors accuracy is documented in 5 points test report prepared by firma Keller Druckmesstechnik. In order to create a vacuum at both reactors, ILMVAC P4Z vacuum pump was used. For pumping water or aqueous alkanolamine solutions into reactor, a HPLC pump (KNAUER Smartline pump 100, 50 ml min⁻¹) was used. However, due to change in viscosity of the aqueous alkanolamine solutions, density of each solution was measured prior to pumping, with use of pycnometer corrected to three decimal places with thermometer (Assistant 2572/325, volume of 25.003 cm³ in 293.15 K), and the pumped amount was controlled gravimetrically (Sartorius BL1500S).

The data measured by sensors are collected in U12 LabJack measurement and automation device, which is an interface between computers and the physical world. Afterwards collected data are sent via a Wi-Fi network at a PC workstation, where pressure and temperature of both reactors are recorded in a program, in ProfiLab environment. The recording interval can be determined in a range of 1 to 10000 seconds.

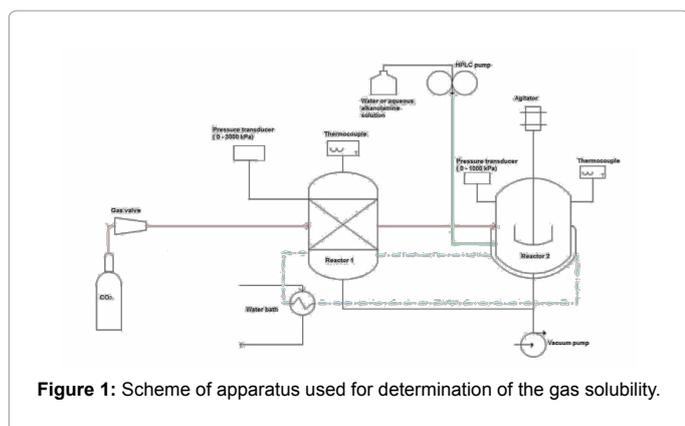


Figure 1: Scheme of apparatus used for determination of the gas solubility.

In addition to measuring the gas solubility, mixture's liquid heat capacity was measured with use of differential scanning calorimeter (Netzsch DSC 204 F1 Phoenix).

Measuring procedure: Initially the apparatus' functionality and accuracy was verified. In order to do so, solubility of CO₂ in water was measured at temperature of 292.95 K, pressure range of 500 up to 1200 kPa, and compared to the literature. The results are presented in section 3.1.1. The standard measuring procedure always starts with generating vacuum in both reactors, and simultaneously heating them up to a desired temperature. After reaching vacuum condition and constant temperature, reactors remained as such for 1 hour, to verify no pressure and temperature change, in order to confirm system's tightness. Afterwards CO₂ was introduced into the first reactor (Figure 1), and the second reactor was filled with 0.225 dm³ of water or amine solution. After obtaining desired temperature and steady pressure readings, CO₂ was introduced to the second reactor. Simultaneously the agitator was started. In the second reactor pressure increased (introducing CO₂) was observed, followed by pressure decrease (absorption process). The end of absorption process is indicated by a constant pressure in the second reactor, and the reaction's duration depends on the solvent and loading. However, to guarantee high accuracy of the results, each experiment lasted minimum one day, with agitator on during the whole measurement, despite equilibrium pressure was often obtained earlier. Each measurement was repeated, and also the correlation between points obtained was controlled.

In order to measure heat capacity with use of differential scanning calorimeter, for each measurement baseline profile (empty sample pan), a standard sample profile (24.9 mg sapphire standard), and a sample profile, as further described in [18,19], were determined. Additionally, measuring method was prepared for this application, where starting temperature was 293.15 K, followed by heating (heating rate 5 K min⁻¹) to 298.15 K, and then it is kept isothermally for 10 min, before the final heating to 355.15 K (heating rate 40 K min⁻¹), which is again followed by isothermal step for 10 min. Afterwards, cooling to 298.15 K was applied, allowing cp calculation during cooling step. Each measurement was prepared as triplicates.

The method is in line with Netzsch [19] recommendation, and the results were analysed using the Proteus Analysis (version 6.1) data analysis program.

CO₂ solubility calculation: The solubility determination is based on approach presented by Park and Sandall [20]. However the calculation is modified, since Peng Robinson Equation of State (PREOS) [21] is used, available in ASPEN Plus™ V8.0 simulation software, rather than compressibility factors. As a consequence, number of CO₂ moles (n_{1CO₂}) in the first reactor (Figure 1) just before feeding the gas to the second reactor (but after obtaining constant pressure and temperature in the first reactor) is calculated with use of PREOS. After introducing the gas to the second reactor, and obtaining constant pressure and temperature in the first reactor, n_{2CO₂} is calculated with PREOS. Finally number of CO₂ moles (n_{1CO₂}) introduced is calculated by subtracting n_{2CO₂} from n_{1CO₂}. The equilibrium pressure, obtained from the second reactor, is used for calculating the amount of remaining CO₂ (n_{eCO₂}). Finally, number of moles absorbed is calculated by subtracting remaining CO₂ moles (n_{eCO₂}) from introduced CO₂ moles (n_{1CO₂}):

$$n_{CO_2}^{abs} = (n_{CO_2}^1 - n_{CO_2}^2) - n_{CO_2}^e = n_{CO_2}^i - n_{CO_2}^e \quad (1)$$

Modelling of gas solubility

Physical solubility: Phase equilibria are described with use

of fugacity coefficient in the following relations of vapour-liquid equilibrium [22]:

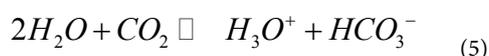
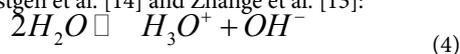
$$x_i \phi_i^L = y_i \phi_i^V \quad (2)$$

Where fugacity coefficients are describing deviation from ideal gas behaviour are applied despite standard fugacity and activity coefficients. Moreover, fugacity coefficients can be calculated with use of cubic equations of state. However, because weak electrolytes are considered in this research, approach with Henry constant as standard fugacity was used instead [22]:

$$P \cdot Y_1 \cdot \phi_1 = H_{12} \cdot X_1 \cdot \gamma_1^* \quad (3)$$

Where system pressure (P), mole fraction in vapour phase (y_1) and in liquid phase (x_1), Henry's law constant of solute (1) in solvent (2) (H_{12}), fugacity coefficient in vapour phase (ϕ_1), and activity coefficient of solute in the solvent (γ_1^*) are included, as further described by Gmehling [22]. In this research fugacity coefficient was calculated with use of Redlich-Kwong EOS [22], activity coefficient was determined with use of electrolyte Non Random Two Liquid model, and coefficients for Henry constant of 2-(Ethylamino) ethanol, were based on diglycolamine (DGA) from [23].

Chemical solubility: The chemical solubility, which is the chemical equilibrium for the aqueous phase chemical reactions between water, amines, acid gases (e.g. CO₂), together with physical solubility are representing the overall acid gases solubility in aqueous amines solutions. These equilibrium reactions were developed for 2-(Ethylamino) ethanol, and are based on reactions presented by Austgen et al. [14] and Zhange et al. [13]:



Reactions describe ionization of water (4), dissociation of carbon dioxide (5) and bicarbonate (6), and amine protonation (7). In addition to that, carbamate reversion to bicarbonate, firstly proposed by Caplow [24], is also included in the chemical solubility, which is only possible for primary and secondary amines [13,14]:



Equilibrium constants for reactions 4 - 8 are presented as temperature dependent via:

$$\ln(K) = C_1 + \frac{C_2}{T} + C_3 \cdot \ln(T) + C_4 \cdot T \quad (9)$$

where the values for each reaction are presented in Table 1.

The Electrolyte-NRTL: Activity coefficient necessary for physical solubility calculation is acquired, when excess Gibbs energy is present [22]. The Electrolyte-NRTL (eNRTL), an excess Gibbs energy expression, presented by Chen and Evans [25], extended by Mock et al. [26] to mixed solvent electrolyte systems is implemented in ASPEN Plus® V8.0 engineering software as ELECNRTL [27] and used in this research. The proposed eNRTL model is a sum of two contributions. The first one is a long-range contribution, describing ion-ion interactions' outside the immediate neighbourhood of central ionic species. For this

Reaction	C ₁	C ₂	C ₃	C ₄	Source
4	132.899	-13445.9	-22.4773	0.0	[38]
5	216.049	-12431.70	-35.4819	0.0	[39]
6	1.6957	-8431.64	0.0	0.005037	[40]
7	231.465	-12092.10	-36.7816	0.0	[39]
8	8.8334	-5274.40	0.0	0.0	[32]

Table 1: Equilibrium constants for reactions [4-8].

contribution Chen and Evans [25] implemented Pitzer's reformulation of the Debye-Huckel formula [28], and the Born expression [29], which includes the difference between the dielectric constants of solvent mixture and water [22]. On the other side, the Non-Random Two Liquid theory developed by Renon and Prausnitz [30], based on the theory of like-ion repulsion and electroneutrality, represents the local contribution, resulting in [14,27]:

$$g^E = g_{Debye-Huckel}^E + g_{Born}^E + g_{NRTL}^E \quad (10)$$

According to Austgen et al. [14] the adjustable parameters required by the eNRTL are only the NRTL binary energy interaction parameters, where, following the theory of like-ion repulsion and electroneutrality, three types of interaction can be determined: molecule - molecule, molecule - ion pair (also ion pair - molecule), and ion pair - ion pair. However, as indicated by Chen and Evans [25] ion pair - ion pair parameters can be set to zero, because no significant impact on vapour-liquid equilibrium (VLE) is then caused. Moreover, because the experimental VLE data do not include in situ analysis of the VLE's composition, only the molecule-molecule binary interaction parameters were determined. Following the literature [14,25,26] all water - ion pair, and ion pair-water binary parameters were kept at default values (8 and -4). In addition, all other binary parameters (alkanolamine - ion pair; ion pair - alkanolamine; acid gas - ion pair; and ion pair - acid gas) were kept at values of 15 and -8. Besides that, binary interaction parameters for water and carbon dioxide (molecule - molecule interaction) are also already determined by Chen and Evans [25].

The non-randomness factor (α) for water - ion pair and for molecule - molecule interactions was fixed at 0.2, as recommended by Chen and Evans [25], and as proposed by Mock et al. [26] it was kept at value of 0.1 for alkanolamine - ion pair and acid gas - ion pair.

The binary energy interaction parameters included in ASPEN Plus® V8.0 are adopted as a temperature dependent as given by Austgen et al. [14]:

$$\tau = a + \frac{b}{T} \quad (11)$$

Values of a and b for alkanolamine - water and water - alkanolamine interactions were determined with use of Data Regression System (DRS). Following path proposed by Austgen et al. [14], for determination of the interaction parameters the Deming algorithm was used, and as an objective function maximum likelihood was selected. The binary energy interaction parameter τ and the nonrandomness parameter α are used for calculating Gibbs energy [22]:

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (12)$$

Pure component properties: Most of the pure component parameters' for 2-(Ethylamino) ethanol were acquired from NIST Databank [31]. However, due to the limited number of data on EAE, it was decided to follow Austgen [32] concept, where the dielectric constants for pure diglycolamine (DGA) was set equal to dielectric constants for diethanolamine (DEA), due to missing data. Therefore coefficients for Henry's constants [23], the dielectric constants [32], equilibrium [14] and kinetic constants [16] were based on DGA [15]. Parameters for CO₂ and H₂O were acquired from ASPEN Plus[®] databanks (APV80.PURE27 and APV80.Binary).

Results and Discussion

Experimental results

Assessment of the apparatus precision: Aim of this article is to provide precise experimental results on CO₂ solubility in aqueous EAE solutions acquired with apparatus described in section 2.1.2. Therefore, in order to ensure correct functionality of the apparatus, and high accuracy of the experimental results, solubility of CO₂ in water was measured at temperature of 292.95 K, pressure range of 500 up to 1200 kPa, and compared to the literature found in Dortmund Data Bank[®] (DDBST GmbH): Silkenbäumer et al. [33], Crovetto [34], Landolt-Börnstein [35], and Addicks et al. [36] The results are presented as a Figure 2, indicating very good fit.

Solvent characteristics

Density: As explained in section 2.1.2., due to change in viscosity of the aqueous alkanolamine solutions, prior to each filling of the second reactor (Figure 1) with the solution, its' density was measured. The averaged density of 2,5 mass % solution was measured to be 0.9969 (± 0.1 mass%), and the averaged density of 5 mass % solution was measured to be 0.9959 (± 0.1 mass%).

Mixture's liquid heat capacity: The binary NRTL interaction parameters are necessary prior to eNRTL model's application for activity coefficient calculations, which are then used for aqueous phase chemical equilibrium, phase equilibrium, enthalpy of absorption, liquid enthalpy and liquid heat capacity determination [14]. However, accurate prediction of mixture's liquid heat capacity is necessary for correct calculation of desorption step, necessary for complete assessment of industry upgrading installations. Therefore liquid heat capacity of pure EAE was measured and compared to the literature [37,38]. Together with aqueous solutions results are presented as a

Figure 3 (with $\pm 3\%$ uncertainty). In addition to that, experimental mixtures' liquid heat capacity is also compared to the simulation, and is presented as a Figure 3. However, because used calorimeter was cooled with air, therefore precise measurement in the lower temperature range was not possible, as can be seen on the graph. The results were used for regressing CPIG Parameters given in Table 2, and used for calculating results on the Figure 3.

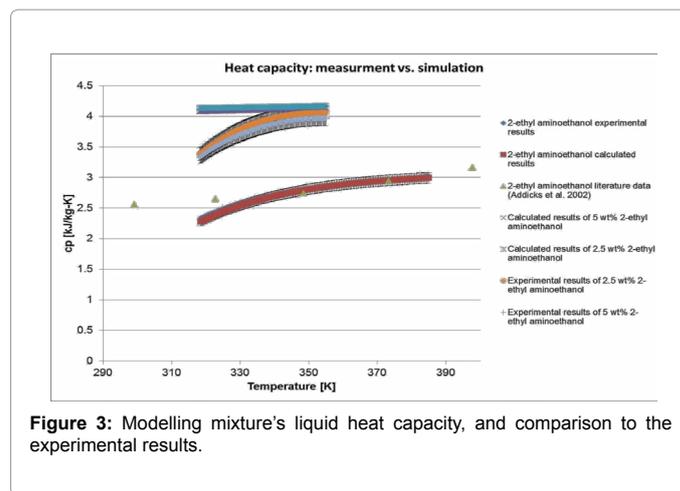


Figure 3: Modelling mixture's liquid heat capacity, and comparison to the experimental results.

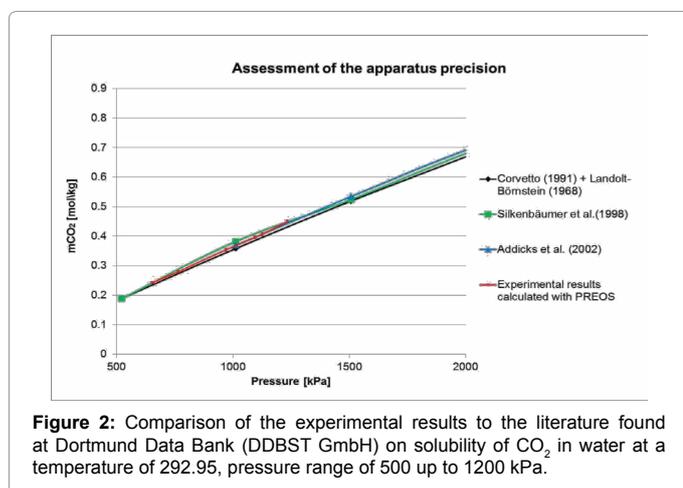


Figure 2: Comparison of the experimental results to the literature found at Dortmund Data Bank (DDBST GmbH) on solubility of CO₂ in water at a temperature of 292.95, pressure range of 500 up to 1200 kPa.

Component	2-ethyl aminoethanol	Standard deviation
Temperature Unit	[C]	[-]
Property Unit	[kJ kmol ⁻¹ K ⁻¹]	
Coefficient 1	-1,58E+02	1.79E+03
Coefficient 2	9,98E+00	5.15E+00
Coefficient 3	-1,42E-01	5.21E+00
Coefficient 4	1,14E-03	4.18E-02
Coefficient 5	-4,98E-06	1.27E-04
Coefficient 6	9,49E-08	1.39E-07
Coefficient 7	-2,73E+02	-
Coefficient 8	7,27E+02	-
Coefficient 9	0,00E+00	-
Coefficient 10	0,00E+00	-
Coefficient 11	0,00E+00	-

Table 2: Temperature dependent coefficients of ideal gas heat capacity equation (CPIG) [14,15].

Results of solubility measurement

Experimental range was decided to be from 289 to 1011 kPa, at 293.00 K, 313.15 K, and 333.15 K. The solvent consisted of in 2.5 mass % and 5 mass % aqueous alkanolamine (Table 3). For each chosen temperature and concentration, presented data consists of five points, hence of five end pressures. Due to the measuring procedure, specifically filling of the first reactor with use of regular pressure regulator at the gas bottle, it was impossible to exactly repeat each measurement. Moreover, correction of the moles of carbon dioxide in the first reactor with use of the gas release valves was also attempted but did not deliver accurate results. As a consequence, for each chosen temperature and concentration minimum 10 measurements were conducted, and the five presented points were chosen based on standard deviation from the results obtained.

Thermodynamic Modelling

Carbamate stability parameters

Suda et al. [7] conducted NMR measurements for EAE, where

he indicated that EAE is forming moderate stability carbamate. An assessment of parameters used for the reduced power law expression, which were set equal to parameters used for DGA [15], was conducted, indicating a very good correlation with Suda et al.'s [7] research result, therefore it was decided not to modify used parameters.

NRTL's binary interaction parameters

Regressed values of the NRTL binary interaction parameters used for local contribution in eNRTL model are included in Table 4. Evaluation of the new values' applicability in representing the experimental results from Table 3 is reported as a Figure 4.

Summarizing, it can be stated that a good fit between model and experimental results was achieved, especially taking under consideration limited data, and pragmatic approach of fitting values from DGA for EAE.

Conclusion

To support model calculation of carbon capture with use of

Parameter	T	2.5 mass % EAE			5 mass % EAE		
		Loading	PCO2	Uncertainty	Loading	PCO2	Uncertainty
Unit	[K]	[mol CO ₂ mol EAE ⁻¹]	[kPa]	[kPa]	[mol CO ₂ mol EAE ⁻¹]	[kPa]	[kPa]
	293.00	1.4105	314	±1	1.1270	405	±1
	293.00	1.7591	541	±1	1.2222	514	±1
	293.00	1.9493	653	±1	1.2698	552	±1
	293.00	2.1078	71	±1	1.4841	721	±1
	293.00	2.5832	1011	±1	1.5873	840	±1
	313.15	1.1569	289	±1	1.0238	410	±1
	313.15	1.3154	416	±1	1.1905	668	±1
	313.15	1.4263	523	±1	1.2619	750	±1
	313.15	1.5214	561	±1	1.3730	856	±1
	313.15	1.5689	637	±1	1.3968	946	±1
	333.15	1.1569	444	±1	1.1032	713	±1
	333.15	1.2520	524	±1	1.1270	723	±1
	333.15	1.4263	653	±1	1.1905	790	±1
	333.15	1.6323	786	±1	1.2540	890	±1
	333.15	1.7116	852	±1	1.3492	1010	±1

Table 3: CO₂ solubility in 2-(Ethylamino)ethanol (EAE).

Parameter	Component i	Component j	Value	Standard deviation
A	H ₂ O	EAE	16.514	0.128
A	EAE	H ₂ O	-3.958	0.026
B	H ₂ O	EAE	-16.141	40.443
B	EAE	H ₂ O	-3.211	8.031

Table 4: NRTL's binary interaction parameters obtained with use of ASPEN Plus® V8.0 Data Regression System (DRS).

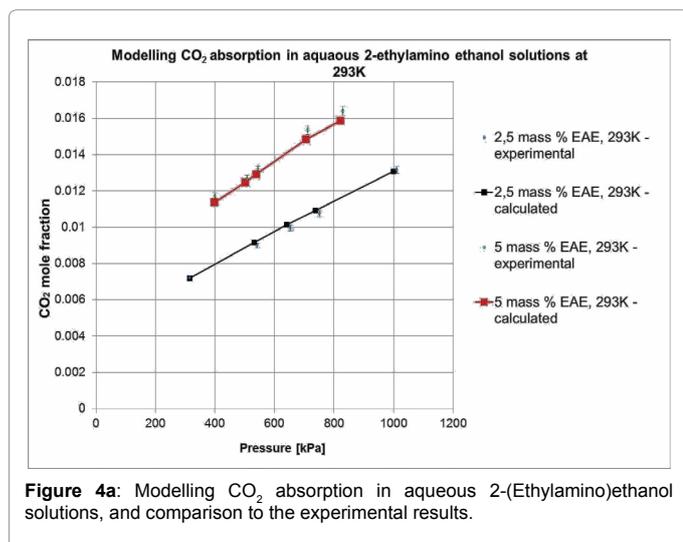


Figure 4a: Modelling CO₂ absorption in aqueous 2-(Ethylamino)ethanol solutions, and comparison to the experimental results.

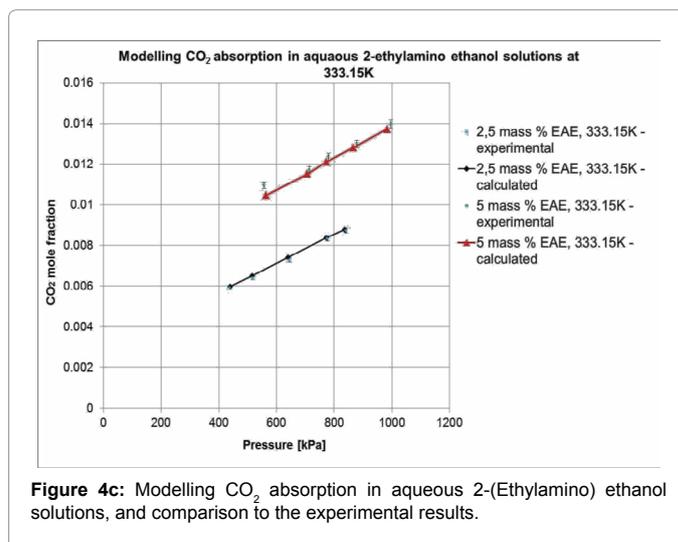


Figure 4c: Modelling CO₂ absorption in aqueous 2-(Ethylamino) ethanol solutions, and comparison to the experimental results.

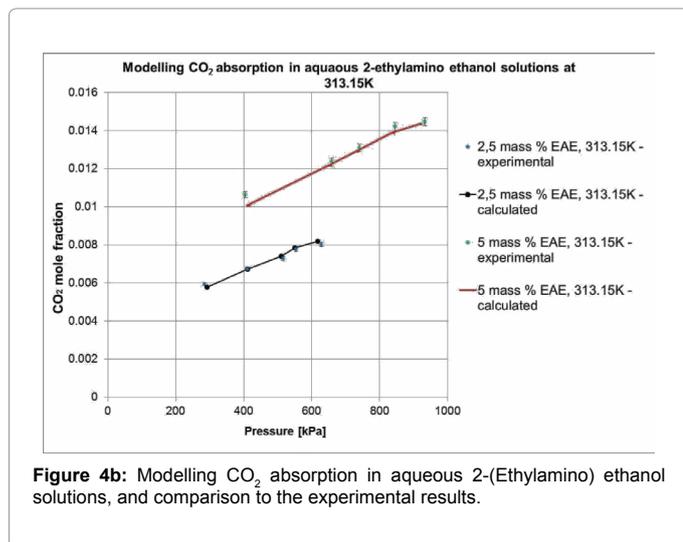


Figure 4b: Modelling CO₂ absorption in aqueous 2-(Ethylamino) ethanol solutions, and comparison to the experimental results.

2-(Ethylamino) ethanol, a promising alternative to diethanolamine (DEA) or monoethanolamine (MEA) was analysed, NRTL's binary interaction parameters necessary for eNRTL model, which can be used for modelling EAE's performance have been regressed. EAE's performance was modelled with use of eNRTL model indicating a good fit between experimental and simulation results (Figure 4). Model based optimization of the biogas power plants to biomethane power plants with use of 2-(Ethylamino) ethanol, for which the main raw material can be bio-ethanol, is now possible. The further research will focus on

advanced economic and ecological analysis of the biogas upgrading with use of amine absorption processes.

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