

Experimental Investigation of Reactive Absorption of Ammonia and Carbon Dioxide by Carbonated Ammonia Solution

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ABSTRACT: *In this work, reactive absorption of gases in aqueous electrolyte solutions has been investigated resulting in the development of a procedure in order to calculate the concentrations of ionic and molecular species in the liquid phase. Two duplicate experiments were conducted to investigate simultaneous reactive absorption of ammonia and carbon dioxide in partially carbonated ammonia solutions. The experiments were carried out employing an absorption pilot plant. The compositions of the electrolytes (ammonia and carbon dioxide groups) have been determined using principle knowledge of electrolyte solutions. The results revealed that the concentrations of ionic and molecular species in the liquid phase drastically influence the absorption rates of ammonia and carbon dioxide.*

KEY WORDS: *Reactive absorption, Electrolytes solutions, Experimental investigation, Ammonia, Carbon dioxide.*

INTRODUCTION

In the last decades, one of the most important goals of environmental efforts has been removal of the undesirable gases from output gas streams of steel, cement, chemical and petrochemical industries [1-5]. Some techniques such as reactive absorption, membrane separation and CO₂ fixation by microbes have been used for this purpose [5]. Chemical absorption seems to be the most practical and effective technique. Chemical absorption is an important unit of several chemical and petrochemical industries.

Chemical reactions in the absorption of undesirable gases bring many advantages in terms of operating conditions such as increasing mass transfer while decreasing the operating total pressure [5-6].

Recently several important industrial reactive absorption processes have been successfully investigated both theoretically and experimentally by a number of researchers [5-15]. Usually reactive absorption processes occur in aqueous solutions of electrolytes. In these

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solutions the components are in ionic and molecular form whereas in the gas phase the components are only in molecular form. The ionic species affect the level of acidity and basicity of the liquid phase, which has an impact on the absorption rate of the gases especially on acid and base gases like CO₂ and NH₃. The previous researches have not considered the effects of all species in liquid and gas phases on absorption of the components [14-16].

Experimental investigation of reactive absorptions can lead to better understanding of the process behavior and designing more efficient operating conditions. Therefore, in this work, a procedure has been introduced to study reactive absorption processes with aqueous electrolyte solutions applying the principles of electrolytes solutions [16-18]. In addition, as a case study, simultaneous reactive absorption of carbon dioxide and ammonia has experimentally been investigated. Moreover, all ionic and molecular species concentration profiles along the column height have been obtained. Furthermore, the influence of ionic and molecular species on absorption rate of the components has been studied.

Modeling of electrolyte systems

Thermodynamical models of electrolyte systems composed of water as solvent as well as dissolved electrolytes include the following equations [17]:

1- Overall mass balance of electrolytes:

$$m_A = m_a + (m_+ + m_-)/2 \quad (1)$$

2- Charge balance (Electroneutrality of the solution):

$$m_+ + m_- \quad (2)$$

3- Equilibria of chemical reactions taking place in the solution (dissociation of water and electrolytes and reactions between electrolytes and/or products of their dissociation) with the deviations from the ideal solution properties taken into account:

$$K = \frac{m_+ \cdot \gamma_+ \cdot m_- \cdot \gamma_-}{m_a \cdot \gamma_a} \quad (3)$$

where, K is the association equilibrium constant and γ_+ , γ_- and γ_a respectively represent the activity coefficients of the cation, anion and molecular in aqueous solutions of electrolytes.

Deviations of aqueous electrolyte solution properties from the ideal solution properties are expressed by the means of the excess Gibbs free energy G^E . The classical way of calculating the activity coefficients of real species dissolved in the solution is based on the semi-empirical Pitzer equation for G^E [18-21]:

$$G^E/(n_w RT) = \quad (4)$$

$$f_1(I) + \sum_i \sum_j \{ \beta_{ij}^{(0)} + \beta_{ij}^{(1)} f_2(I) \} m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k$$

where, $f_1(I)$ is the Debye-Huckel-Pitzer function describing the effect of long-range ion-ion electrostatic interactions depending on ionic strength of the solution. $\beta_{ij}^{(0)}$ and $\beta_{ij}^{(1)}$ are the parameters of binary short-range intermolecular interactions. $f_2(I)$ is a function describing the effect of ionic strength, on binary short-range intermolecular interactions. μ_{ijk} is the parameter of ternary short-range intermolecular interactions. Molal activity coefficients of the real species, γ_i , dissolved in the solution and mole activity coefficient of the solvent γ_w are expressed by the following relationships:

$$\ln \gamma_i = \partial [G^E/(n_w RT)] / \partial m_i \quad (5)$$

$$\ln \gamma_w = M_w \partial [G^E/(RT)] / \partial n_w \quad (6)$$

Chemical system of reactive absorption of NH₃ and CO₂

In this work, simultaneous reactive absorptions of NH₃ and CO₂ have been investigated. In this process NH₃ can be absorbed very rapidly, whereas CO₂ is a low soluble gas in the aqueous solutions. However, the reactions in the weak electrolyte system of CO₂ and NH₃ cause an increase in the CO₂ absorption rate. In the liquid phase, there are nine molecular and ionic species concluding NH₃, CO₂, H₂O, NH₄⁺, HCO₃⁻, CO₃²⁻, H⁺, OH⁻ and NH₂COO⁻. The species are in equilibrium with the following chemical reactions [22-23]:





The model of the present system consists of the following equations:

1- Equilibria of chemical reactions

$$K_1 = \frac{m_{\text{NH}_4^+} \cdot \gamma_{\text{NH}_4^+} \cdot m_{\text{OH}^-} \cdot \gamma_{\text{OH}^-}}{m_{\text{NH}_3} \cdot \gamma_{\text{NH}_3} \cdot a_{\text{H}_2\text{O}}} \quad (12)$$

$$K_2 = \frac{m_{\text{H}^+} \cdot \gamma_{\text{H}^+} \cdot m_{\text{HCO}_3^-} \cdot \gamma_{\text{HCO}_3^-}}{m_{\text{CO}_2} \cdot \gamma_{\text{CO}_2} \cdot a_{\text{H}_2\text{O}}} \quad (13)$$

$$K_3 = \frac{m_{\text{H}^+} \cdot \gamma_{\text{H}^+} \cdot m_{\text{CO}_3^{2-}} \cdot \gamma_{\text{CO}_3^{2-}}}{m_{\text{HCO}_3^-} \cdot \gamma_{\text{HCO}_3^-}} \quad (14)$$

$$K_4 = \frac{m_{\text{NH}_2\text{COO}^-} \cdot \gamma_{\text{NH}_2\text{COO}^-} \cdot a_{\text{H}_2\text{O}}}{m_{\text{NH}_3} \cdot \gamma_{\text{NH}_3} \cdot m_{\text{HCO}_3^-} \cdot \gamma_{\text{HCO}_3^-}} \quad (15)$$

$$K_5 = \frac{m_{\text{H}^+} \cdot \gamma_{\text{H}^+} \cdot m_{\text{OH}^-} \cdot \gamma_{\text{OH}^-}}{a_{\text{H}_2\text{O}}} \quad (16)$$

The activity coefficients of the present system have been calculated using *Krop* model that are based on Pitzer equation [24]:

$$G^E / (n_w RT) = f_1(I) + \sum_i \sum_j m_i \cdot m_j \cdot (\beta_{ij}^{(0)} + \beta_{ij}^{(1)} \cdot f_2(I)) + \sum_i \sum_j \sum_k m_i m_j m_k T_{ijk} \quad (17)$$

In this equation, instead of molalities m_i , m_j and m_k of the real species, dissolved in the solution and occurring in the Pitzer equation (4), the molalities m_i , m_j and m_k of the groups of species of the individual electrolytes (sums of molalities of the real species representing all the independent forms of occurrence of the given electrolyte in aqueous solution) have been introduced. In this system, A is the group of ammonia species and C is the group of carbon dioxide species.

Binary $\beta_{ij}^{(0)}$ and $\beta_{ij}^{(1)}$ and ternary T_{ijk} , interaction parameters between the electrolytes, are functions of temperature as reported by *Krop* [24]. The activity

coefficients are obtained by differentiating Eq. (17). Dissociation equilibrium constants are determined using the correlations that are reported by *Brewer* [25-26].

2- Mass balances of the electrolytes:

$$m_A = m_{\text{NH}_3} + m_{\text{NH}_4^+} + m_{\text{NH}_2\text{COO}^-} \quad (18)$$

$$m_C = m_{\text{CO}_2} + m_{\text{CO}_3^{2-}} + m_{\text{HCO}_3^-} + m_{\text{NH}_2\text{COO}^-} \quad (19)$$

3- Charge balance in the solution

$$m_{\text{NH}_4^+} + m_{\text{H}^+} = m_{\text{NH}_2\text{COO}^-} + 2m_{\text{CO}_3^{2-}} + \quad (20)$$

$$m_{\text{HCO}_3^-} + m_{\text{NH}_2\text{COO}^-} + m_{\text{OH}^-}$$

EXPERIMENTAL SECTION

The pilot plant

The scheme of the absorption pilot plant is shown in Fig. 1. The column is made of a 105 mm diameter glass cylinder containing four packing sections. A tray is mounted between these sections to redistribute the liquid flow. On each tray, two temperature sensors are installed to measure gas and liquid temperatures. Liquid and gas samples can also be taken using two valves, which are installed on the trays. The height of each packing section was 650 mm. The packing beads were ceramic Rashing rings with diameter of 0.5 inches. Gas and liquid samples were taken at five points of the column as shown in Fig. 1. Temperatures were measured at five positions along the column to give temperature profiles for gas and liquid phases.

Procedure of the Experiments

Experimental data were obtained in steady state conditions at atmospheric pressure. At the beginning of the experiments, only nitrogen gas was fed to the column then liquid and other gas feed flow rates and temperatures were adjusted to the desired values by four flowmeters. After reaching steady-state conditions, which was indicated by a steady-state temperature profile and fixed concentration of the analyzer, gas and liquid samples were taken. Duplicate liquid and gas samples were taken with a time interval of about 10 minutes. Gas samples were sent to an online gas analyzer and liquid samples were analyzed offline.

Table 1: Operating conditions of absorption column.

Process data	Experiment 1		Experiment 2	
	Feed	outlet	Feed	outlet
Gas				
Temperature [C]	29.9	30.8	28.4	30.3
NH ₃ [mol/hr]	35.30	0.92	36.00	1.58
CO ₂ [mol/hr]	41.0	28.7	41.9	27.2
N ₂ [mol/hr]	191.2	191.2	195.8	195.8
H ₂ O [mol/hr]	0	13.6	0	12.6
Liquid				
Temperature [C]	30.4	33.5	29.6	33.3
NH ₃ [mol/m ³]	290	577	545	829
CO ₂ [mol/m ³]	71.9	174.2	173	296

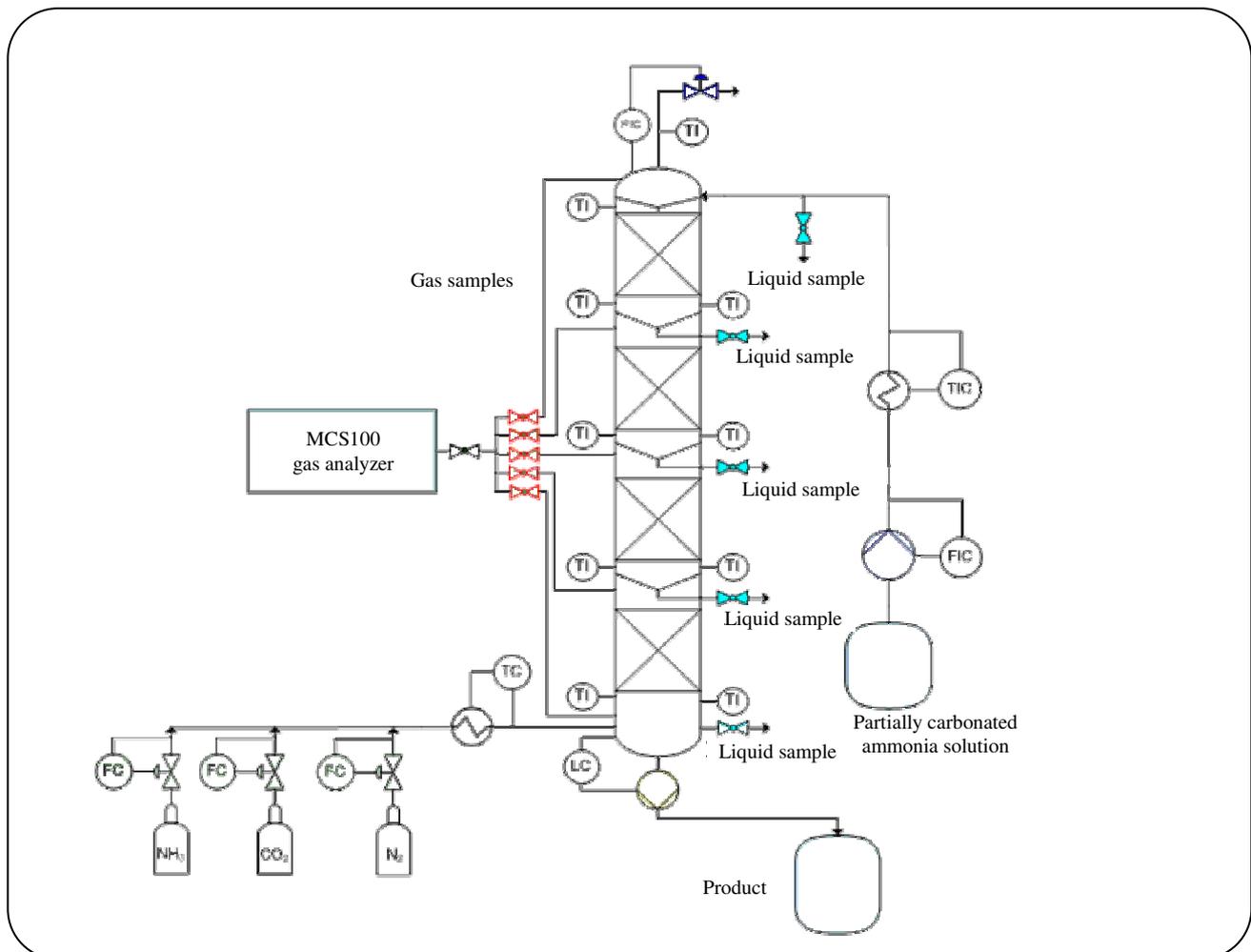
**Fig. 1: The scheme of the absorption pilot plant.**

Table 2: Temperatures and component concentrations of pilot plant experiment.

Section height Z[m]	Gas component mole fractions [Pressure/total Pressure]				Temperature [C]		Liquid concentration [Mole/m ³]	
	N ₂	CO ₂	NH ₃	H ₂ O	T _G	T _L	m _A	m _C
Experiment 1								
2.60	0.8157	0.1225	0.0039	0.0579	30.8	30.4	290.3	71.9
1.95	0.8021	0.1344	0.0033	0.0602	31.2	30.6	292.8	99.8
1.30	0.7923	0.1451	0.0024	0.0602	31.6	31.0	296.1	124.6
0.65	0.7852	0.1499	0.0018	0.0631	31.8	31.2	297.0	137.0
0.00	0.7148	0.1532	0.1320	0.0000	29.9	33.5	576.9	174.2
Experiment 2								
2.60	0.8255	0.1147	0.0067	0.0531	30.3	29.6	545.0	173.0
1.95	0.8097	0.1284	0.0061	0.0557	30.8	29.9	548.9	205.0
1.30	0.7988	0.1382	0.0048	0.0581	31.1	30.4	547.0	228.7
0.65	0.7868	0.1498	0.0038	0.0597	31.5	30.8	548.0	256.9
0.00	0.7158	0.1534	0.1308	0.0000	28.4	33.3	833.2	297.5

Pilot plant experiments have been carried out in different conditions in terms of inlet liquid phase concentrations. Liquid flow rate was 120 L/h for all of the experiments. Inlet and outlet experimental conditions of the absorption column are given in Table 1.

Measurements

The liquid samples were analyzed offline with an ion chromatography (IC-762 type from Metrohm company) based on conductivity detection method. As mentioned above, the results are averages of two samples that are taken at the same condition but at different times. Here the average deviation for the determination of CO₂ and NH₃ was in the range of 4-6%.

The online gas analyzer is a MCS100 from Sickmaihak Company, which is an extremely compact multi-component infrared photometer for extractive continuous monitoring of flue gases. In this process H₂O, NH₃ and CO₂ concentrations were measured. Response time of MCS100 analyzer is less than 2 seconds with average measurement deviation (precision) of less than 2% for NH₃ and CO₂.

RESULTS AND DISCUSSION

Table 2 shows the temperatures and component concentrations of experiments 1 and 2. The solubility of ammonia and carbon dioxide in aqueous solutions are very different. The results of Table 2 indicate that almost all of the ammonia has been absorbed at the bottom section of the column whereas carbon dioxide has been absorbed throughout the column. The Table 2 shows that in experiment 2, the amount of absorbed CO₂ in section one (at the top of the column) is 32 mole/h whereas at the section 3 it is 28 mole/h. However, by increasing basicity and free ammonia of the solution at the bottom of the column, CO₂ absorption rate increases to 40 mol/hr. This explains the effects of basicity and free ammonia concentration on CO₂ absorption rate.

The experiments were conducted to study the impacts of liquid feed concentration on CO₂ and NH₃ absorption. Table 2 shows partial pressure of NH₃ at the gas outlet increases by raising NH₃ concentration in the liquid feed. In this table mole fraction of NH₃ at the gas outlet were 0.0039 and 0.0067 for experiments 1 and 2 respectively.

The results of Table 2 revealed that absorption of CO_2 increases as a result of an increase to the NH_3 concentration in the liquid feed. The amounts of absorbed CO_2 are 12.27 and 14.95 for experiments 1 and 2 respectively.

Fig 2 shows component mole fractions in gas phase along the column height for experiment 2. It indicates that NH_3 is almost completely transferred to liquid phase at the bottom of the column, while water is transferred from liquid to gas phase. As a result nitrogen partial pressure in the gas phase is increased. CO_2 is gradually transferred to the liquid phase throughout the column. Water concentration curve in Fig. 2 shows that there is no water in the gas feed although when the gas phase enters the column its water content starts to rise due to the mass transfer from the liquid phase to the gas phase.

In the liquid phase there are molecular and ionic species and the composition is obtained using equations of electrolyte systems as mentioned above. Fig. 3 depicts molecular and ionic ammonia species concentrations. At the liquid inlet solution, there are free ammonia molecules. After contacting the two phases the concentration of free molecular ammonia gradually decreases due to the reaction between ammonia and CO_2 . However, at the bottom of the column absorption of ammonia causes an increase in its liquid phase concentration. Ammonia reacts with carbon dioxide producing NH_2COO^- . Therefore, at the bottom due to high concentration of ammonia, NH_2COO^- production is higher than other sections. In Fig. 3, NH_4^+ concentration curve indicates that absorption and reactions of the components increase the amount of NH_4^+ in the liquids phase as the liquid flows from the top to the bottom of the column.

Fig. 4 displays the concentrations of ionic and molecular carbon dioxide species. Carbon dioxide is an acidic gas thus the solution acidity grows by the absorption of CO_2 . Fig. 4 indicates that due to the absorption of CO_2 along the column, the amount of HCO_3^- ascends. However, ammonia is a basic gas thus absorption of ammonia leads to a decrease in the amount of HOC_3^- . The absorption and reaction rates are high at the lowest section of the column, causing an increase in the concentrations of CO_3^{2-} and NH_2COO^- . Throughout the column, the concentration of free CO_2 in the liquid is very low due to its reactions with OH^- , H_2O and NH_3 .

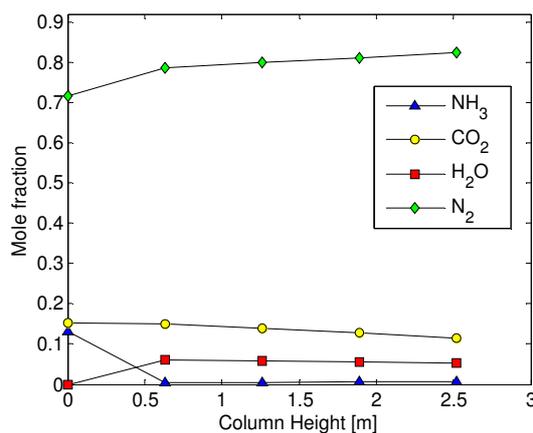


Fig. 2: Gas phase mole fractions along the column height.

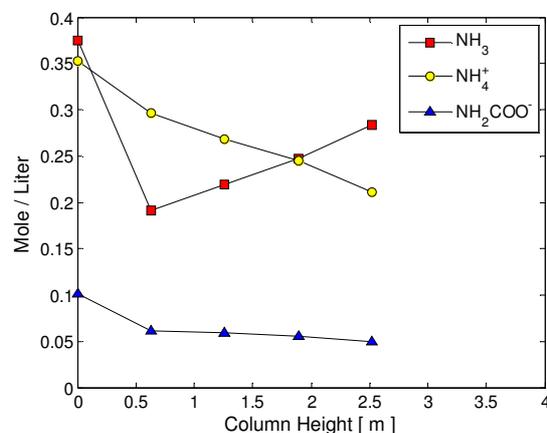


Fig. 3: Concentration of ionic and molecular ammonia species along the column in experiment 2.

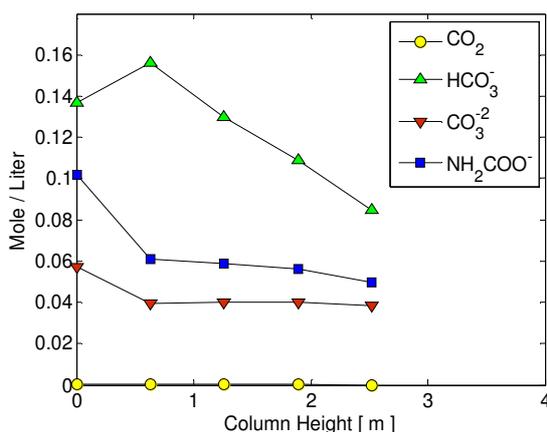


Fig. 4: Ionic and molecular concentration of carbon dioxide species along the column in experiment 2.

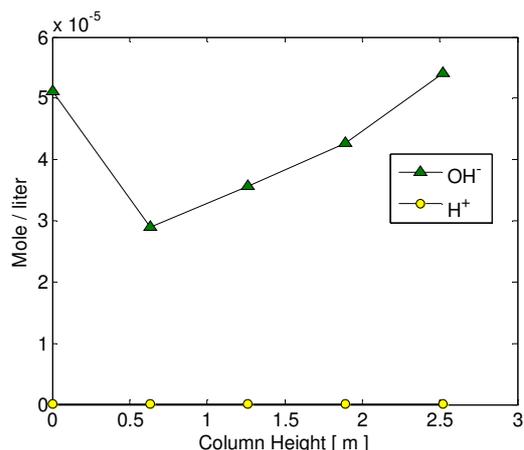


Fig. 5: Acidity and basicity of solution along the column height in experiment 2.

Fig. 5 indicates the acidity and basicity of the liquid phase along the column. The inlet solution is basic thus due to the absorption of acidic gas (CO_2) the basicity of the solution decreases that in turn leads to a lower rate of CO_2 absorption.

Absorption of NH_3 and CO_2 is exothermic, causing high variation in temperature of both phases at the first section of the column. The temperature gradients for both phases are shown in Fig. 6.

CONCLUSIONS

In this work, simultaneous reactive absorption of carbon dioxide and ammonia in partially carbonated ammonia has experimentally been investigated. Electrolyte principles of aqueous solutions have been used to calculate the component concentrations in the liquid phase. Two experiments have been conducted to obtain the data employing a pilot plant absorption column. The experimental results revealed that nearly all of the ammonia was absorbed at the lowest section of the column whereas carbon dioxide absorption occurred gradually throughout the column. The data also indicate carbon dioxide absorption rate strongly depends on the concentrations of free ammonia and hydroxide. In addition, it was revealed that a step up in inlet liquid ammonia concentration would lead to an increase in partial pressure of ammonia at the gas outlet.

Nomenclature

a	Water activity
G	Gibbs energy

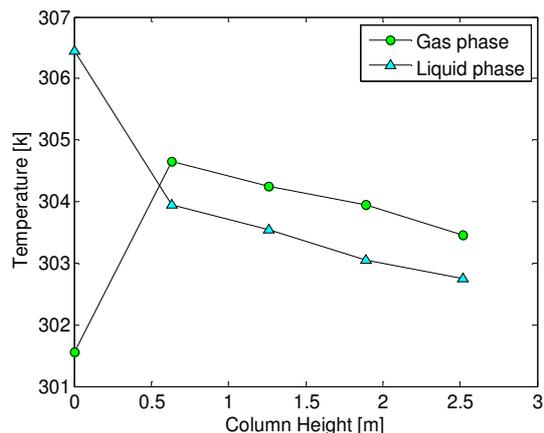


Fig. 6: Temperature gradients of liquid and gas phases along the column height in experiment 2.

m	Molarity
M	Water molecular weight
K	Association equilibrium constant
n	Mole number
I	Ionic strength
γ	Activity coefficients
R	World gas constant
T	Temperature

Superscript

E	Excess characteristic
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Subscripts

A	Ammonia group
a	Molecular aqueous solutions
c	Carbon dioxide group
-	Anion
+	Cation
i,j,k	Components
w	Water

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