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

Ghaemi, Ahad; Shahhosseini, Shahrokh*+

Faculty of Chemical Engineering, Iran University of Science and Technology, P.O. Box 16765-163 Tehran, I.R. IRAN

Ghannadi Maragheh, Mohammad

Nuclear Fuel Cycle School, Nuclear Science and Technology Research Institute, P.O. Box 14155-1339 Tehran, I.R. IRAN

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 CO_2 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

^{*} To whom correspondence should be addressed. +E-mail: shahrokh@iust.ac.ir 1021-9986/11/2/43 8/\$/2.80

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 CO_2 and NH_3 . 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:

$$m_{\rm A} = m_{\rm a} + (m_+ + m_-)/2 \tag{1}$$

2- Charge balance (Electroneutrality of the solution): $m_+ + m_-$ (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:

$$K = \frac{m_{+} \cdot \gamma_{+} \cdot m_{-} \cdot \gamma_{-}}{m_{a} \cdot \gamma_{a}}$$
(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]:

$$G^{E} / (n_{w} RT) =$$

$$f_{1}(I) + \sum_{i} \sum_{j} \left\{ \beta_{ij}^{(0)} + \beta_{ij}^{(1)} f_{2}(I) \right\} m_{i} m_{j} +$$

$$\sum_{i} \sum_{j} \sum_{k} \mu_{ijk} m_{i} m_{j} m_{k}$$
(4)

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:

$$\ln \gamma_{i} = \partial \left[G^{E} / (n_{w} RT) \right] / \partial m_{i}$$
(5)

$$\ln \gamma_{\rm w} = M_{\rm w} \partial \left[G^{\rm E} / (RT) \right] / \partial n_{\rm w} \tag{6}$$

Chemical system of reactive absorption of NH₃ and CO₂

In this work, simultaneous reactive absorptions of NH_3 and CO_2 have been investigated. In this process NH_3 can be absorbed very rapidly, whereas CO_2 is a low soluble gas in the aqueous solutions. However, the reactions in the weak electrolyte system of CO_2 and NH_3 cause an increase in the CO_2 absorption rate. In the liquid phase, there are nine molecular and ionic species concluding NH_3 , CO_2 , H_2O , NH_4^+ , HCO_3^- , CO_3^{2-} , H^+ , OH^- and NH_2COO^- . The species are in equilibrium with the following chemical reactions [22-23]:

$$H_2O \xleftarrow{K_1} OH^- + H^+$$
(7)

$$NH_3 + H_2O \xleftarrow{K_2} NH_4^+ + OH^-$$
(8)

$$\operatorname{CO}_2 + \operatorname{OH}^- \xleftarrow{K_3} \operatorname{HCO}_3^-$$
(9)

$$HCO_{3}^{-} \xleftarrow{K_{4}} H^{+} + CO_{3}^{-2}$$
(10)

$$\mathrm{NH}_3 + \mathrm{HCO}_3^- \xleftarrow{\mathrm{K}_5} \mathrm{NH}_2 \mathrm{COO}^- + \mathrm{H}_2 \mathrm{O}$$
(11)

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

1- Equilibria of chemical reactions

$$K_{1} = \frac{m_{NH_{4}^{+}} \cdot \gamma_{NH_{4}^{+}} \cdot m_{OH^{-}} \cdot \gamma_{OH^{-}}}{m_{NH_{4}} \cdot \gamma_{NH_{4}} \cdot a_{H_{2}O}}$$
(12)

$$K_{2} = \frac{m_{H^{+}} \cdot \gamma_{H^{+}} \cdot m_{HCO_{3}^{-}} \cdot \gamma_{HCO_{3}^{-}}}{m_{CO_{2}} \cdot \gamma_{CO_{2}} \cdot a_{H_{2}O}}$$
(13)

$$K_{3} = \frac{m_{H^{+}} \cdot \gamma_{H^{+}} \cdot m_{CO_{3}^{-2}} \cdot \gamma_{CO_{3}^{-2}}}{m_{HCO_{3}^{-2}} \cdot \gamma_{HCO_{3}^{-2}}}$$
(14)

$$K_{4} = \frac{m_{NH_{2}COO^{-}} \cdot \gamma_{NH_{2}COO^{-}} \cdot a_{H_{2}O}}{m_{NH_{3}} \cdot \gamma_{NH_{3}} \cdot m_{HCO_{3}^{-}} \cdot \gamma_{HCO_{3}^{-}}}$$
(15)

$$K_{5} = \frac{m_{H^{+}} \cdot \gamma_{H^{+}} \cdot m_{OH^{-}} \cdot \gamma_{OH^{-}}}{a_{H_{2}O}}$$
(16)

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

$$G^{E} / (n_{w} RT) =$$

$$f_{1}(I) + \sum_{i} \sum_{j} m_{i} \cdot m_{j} \cdot (\beta_{ij}^{(0)} + \beta_{ij}^{(1)} \cdot f_{2}(I)) +$$

$$\sum_{i} \sum_{j} \sum_{k} m_{i} m_{f} m_{k} T_{ijk}$$
(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:

$$m_{A} = m_{NH_{3}} + m_{NH_{4}^{+}} + m_{NH_{2}COO^{-}}$$
(18)

$$m_{\rm C} = m_{\rm CO_2} + m_{\rm CO_3^{-2}} + m_{\rm HCO_3^{-1}} + m_{\rm NH_2COO^{-1}}$$
(19)

3- Charge balance in the solution

$$m_{\rm NH_4^+} + m_{\rm H^+} = m_{\rm NH_2COO^-} + 2m_{\rm CO_3^{-2}} +$$
(20)
$$m_{\rm HCO_7^{-1}} + m_{\rm NH_2COO^{-1}} + m_{\rm OH^{-1}}$$

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 analyzed offline.

Process data	Experin	ment 1	Experiment 2		
Tiocess data	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	

Table 1: Operating conditions of absorption column.



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

Section height	Gas compo	onent mole fractior	ns [Pressure/total	Pressure]	Tempera	ture [C]	Liquid co [Mo]	ncentration le/m ³]
Z[m]	N_2	CO_2	NH ₃	H_2O	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

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

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 CO_2 and NH_3 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 H_2O , 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 CO_2 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, CO_2 absorption rate increases to 40 mol/hr. This explains the effects of basicity and free ammonia concentration on CO_2 absorption rate.

The experiments were conducted to study the impacts of liquid feed concentration on CO_2 and NH_3 absorption. Table 2 shows partial pressure of NH_3 at the gas outlet increases by raising NH_3 concentration in the liquid feed. In this table mole fraction of NH_3 at the gas outlet were 0.0039 and 0.0067 for experiments 1 and 2 respectively. Ghaemi A. et al.

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 CO2. However, at the bottom of the column absorption of ammonia causes an increase in its liquid phase concentration. Ammonia reacts with carbon dioxide producing NH2COO. Therefore, at the bottom due to high concentration of ammonia, NH₂COO⁻ production is higher than other sections. In Fig. 3, NH₄⁺ 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_2^{-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.

Excess characteristic



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 (CO₂) 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.

Molarit	m
Water molecular weigh	М
Association equilibrium constar	Κ
Mole numbe	n
Ionic strengt	Ι
Activity coefficient	γ
World gas constar	R
Temperatur	Т

Superscript

E

Subscripts

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

Received : Sep. 16, 2008 ; Accepted : Sep. 28, 2010

REFERENCES

- Kohl A., Nielsen R., "Gas Purification", 5th Edition, Gulf Publications Company, (1997).
- [2] Maceiras R., Alvarez E., Angeles M., Effect of Temperature on Carbon Dioxide Absorption in Monoethanolamine Solutions, *Chem. Eng. J.*, **138**, p. 295 (2008).

- [3] Van Loo S., Van Elk E.P., Versteeg G.F., The Removal of Carbon Dioxide with Activated Solutions of Methyl-Diethanol-Amine, *J. Petrol Sci. Eng.*, 55, p. 135 (2007).
- [4] Kloeker M., Kenig E.Y., Hoffmann A., Kreis P., Gorak A., Rate-based Modeling and Simulation of Reactive Separations in Gas/vapour-Liquid Systems, *Chem. Eng. Process*, 44, p. 617 (2005).
- [5] Danckwerts P.V., "Gas Liquid Reactions", McGraw-Hill, New York, (1970).
- [6] Brettschneider O., Thiele R., Faber R., Thielert H., Wozny G., Experimental Investigation and Simulation of the Chemical Absorption in a Packed Column for the System, *Separa. purifica. Technol.*, **39**, p. 139 (2004).
- [7] Asprion N., Nonequilibrium Rate-Based Simulation of Reactive Systems: Simulation Model, Heat Transfer, and Influence of Film Discretization, *Ind. Eng. Chem. Res.*, 45, p. 2054 (2006).
- [8] Taylor R., Krishna R., "Multicomponent Mass Transfer", John Wilrey, New York (1993).
- [9] Yu W.C., Astarita G., Selective Absorption of Hydrogen Sulphide in Tertiary Amine Solutions, *Chem. Eng. Sci.*, 42, p. 419 (1987).
- [10] Thielert H., Simulation und Optimierung der Kokereigaswa Sche, Ph.D. Thesis, Technical University of Berlin, Germany, (1997).
- [11] Kobus A., "Ein Heuristisch-Numerischer Ansatz Zum Systematischen Entwurf und Design von Absorptionsverfahren", VDIVerlag, Dusseldorf, (1999).
- [12] Gandhidasan P., "Heat and Mass Transfer in Solar Regenerators", in: N.P. Cheremisin off (Ed.), Handbook of Heat and Mass Transfer, vol. 2, Gulf Publ. Comp., Houston, pp. 1475-1499 (1986).
- [13] Kenig E.Y., Kholpanov L.P., Katysheva L.I., I.H.Markish, Malyusov V.A., Calculation of Two-Phase Non-Isothermal Absorption in a Liquid Film in Downward co-Current Fow, *Theor. Found. Chem. Eng.*, **19**, p. 97 (1985).
- [14] Noeres C., Kenig E.Y., Gorak A., Modeling of Reactive Separation Processes: Reactive Absorption and Reactive Distillation, *Chem. Eng. Process*, 42, p. 157 (2003).
- [15] Stankiewicz A., "Re-Engineering the Chemical Processing Plant", Marcel Dekker, (2004).

- [16] Ghaemi A., Shahhosseini Sh., Ghannadi M., Nonequilibrium Dynamic Modeling of Carbon Dioxide Absorption by Partially Carbonated Ammonia Solutions, *Chem. Eng. J.*, **149**, p. 110 (2009).
- [17] Edwards T.J., Newman G., Newman J., Prausnitz J.M., "Thermodynamics of Aqueous Solutions Containing Volatile Weak Electrolytes, *AIChE J.*, **21**, p. 248 (1975).
- [18] Pitzer K.S., Thermodynamics of Electrolytes 1. Theoretical Basis and General Equations, J. Phys. Chem., 77, p. 268 (1973).
- [19] Edwards T.J., Maurer G., Newman J., Prausnitz J.M., Vapor-liquid Euilibria in Multicomponent Aqueous Solutions of Volatile Weak Electrolytes, *AIChE J.*, 24, p. 966 (1978).
- [20] Beutier D., Renon H., Representation of NH₃-H₂S-H₂O, NH₃-CO₂-H₂O and NH₃-SO₂-H₂O Vapor-Liquid Equilibria, *Ind. Eng. Chem. Process Des. Dev.*, **17**, p. 220 (1978).
- [21] Chen Ch.Ch., Britt H.J., Boston J.F., Evans L.B., Extension and Application of the Pitzer Equation for Vapor-Liquid Equilibrium of Aqueous Electrolyte Systems with Molecular Solutes, *AIChE J.*, 25, p. 820 (1979).
- [22] Reid R.C., Prausnitz J.M., Poling B.E., "The Properties of Gases and Liquids", McGraw-Hill, New York, (1987).
- [23] Shen J., Yang Y., Maa J., Promotion Mechanism for CO₂ Absorption into Partially Carbonated NH₃ Solutions, *J. Chem. Eng. Japan*, **32**, p. 378 (1999).
- [24] Krop J., New Approach to Simplify the Equation for the Excess Gibbs Free Energy of Aqueous Solution of Electrolytes Applied to the Modeling of the NH₃-CO₂-H₂O Vapor-Liquid Equilibria, *Fluid Phase Equilibria*, **163**, p. 209 (1999).
- [25] Brewer L., "In Flue Gas Desulphurization", Hudson, J. L., Rochelle, G. T.,Ed., ACS Symposium Series 188, American Chemical Society, Washington, DC, (1982) 1-39.
- [26] Brewer L., University of California, Berkeley, Personal Communication, (1986).