Prediction of H_2S and CO_2 Solubility in Aqueous MDEA and MDEA/PZ Solutions Using ELECNRTL and ACID GAS Packages

• **Omid Sabbagh, Maissam Vahidi Ferdowsi, Mohammad Ali Fanaei***
Department of Chemical Engineering, Ferdowsi University of Mashhad, Mashhad, Iran
Corresponding author Email address: fanaei@um.ac.ir

Received: Feb. 24, 2017 / Accepted: Apr. 20, 2017

Abstract

In this study, the solubility of acid gases of hydrogen sulfide and carbon dioxide in MDEA and MDEA/PZ aqueous solutions was evaluated by different thermodynamic packages. Comparison of modeling results with a series of laboratory and industrial data released from 1997 to 2010 indicates the high accuracy of ACID GAS thermodynamic package (Aspen HYSYS 8.3) to prediction of acid gases solubility in the mentioned solutions compared to the ELECNRTL thermodynamic package (Aspen plus V8.2), especially in the range of acid gases operational concentration in the gas refineries.

Keywords: MDEA, PZ, Thermodynamic package, Acid gas solubility, Acid gas, ELECNRTL

1. INTRODUCTION

Sour gas sweetening is one of the most important natural gas refining processes, which is done to remove acid gases such as H_2S and CO_2 in order to reduce the corrosion rate, improve the gas quality, reduce the toxicity of catalysts, etc. Alkanolamines such as MDEA, DEA and mixtures of MDEA/PZ and MDEA/DEA are used as the most common chemical solvents for natural gas sweetening.

Prediction of H_2S and CO_2 solubility in amine solutions is highly essential to design and simulation of natural gas sweetening units. For this purpose, various thermodynamic packages inserted in the popular commercial softwares, such as ASPEN HYSYS and ASPEN PLUS. Two main approaches that are used in these packages are known as "Correlation-Based" and "Activity Coefficient Model-Based". "AMINE" and "APISOUR" packages are examples of the first approach, and "ELECNRTL" and "ACID GAS" packages are examples of the second approach.

Many studies have been done on predicting the solubility of acid gases in amine solutions. Deshmukh and Mather (1981) used the activity coefficients model to predict the solubility of H_2S and CO_2 in amine solutions [1]. Posey et al. (1996) used a simple correlation for prediction of acid gas solubility in alkanolamines [2]. Prashanth Patil et al. (2006) evaluated the solubility of H_2S and CO_2 in MDEA aqueous solution by the extended correlation of Kenneth Eisenberg [3]. Huttenhuis et al. (2009) investigated the Solubility of CO_2 and H_2S in aqueous MDEA solutions, experimentally [4]. Ying Zhang et al. (2011) also examined CO_2 absorption in aqueous MEA and MDEA solutions with electrolyte NRTL model [5, 6].

According to development of chemical process simulators in the last years, many of studies are focused on comparison of them together. Hansen et al. (2011) compared the ASPEN HYSYS and ASPEN PLUS softwares accuracy in predicting of CO_2 absorption by MEA solution [7]. Erik Øi (2012) did a same work but this study was focused on CO_2 removal from exhaust gas [8]. He also compared ASPEN HYSYS and ASPEN PLUS simulation of CO_2 Absorption into MEA from atmospheric gas in the same year [9].

Since 2013, a new option (ACID GAS package) is added to ASPEN HYSYS software that its producer claims this package uses rigorous rate-based calculations and a new property package to deliver unprecedented accuracy and predictive results to amine-based absorption processes [10]. This paper investigates mentioned claim and provides a comparison between the thermodynamic packages of ASPEN PLUS (V8.2) and ASPEN HYSYS (V8.3) in predicting the solubility of acid gases in amine solutions.

2. THEORETICAL FOUNDATIONS

Using thermodynamic relations based on classical concepts of phase equilibriums is an approach resulting in the prediction of acid gases solubility in aqueous alkanolamine solutions. However, the use of parameters such as fugacity and activity is more close to the physical senses than theoretical concept of chemical potential.

For each component in the mixture, the fugacity equality of liquid and vapor phases resulted from thermodynamic equilibrium, provides the possibility of using distinct thermodynamic models for the phases. Therefore, an equation of state will be used for predicting the vapor phase fugacity coefficients, while an activity model is used for the liquid phase. In the following, the calculation methods of vapor-liquid equilibrium condition by equations of state and activity model in thermodynamic packages of ELECNRTL and ACID GAS are discussed.

A. ELECNRTL Thermodynamic Package

One of the methods to predict the equilibrium behavior of electrolyte solutions is the activity coefficient model-based approach, which is established based on calculating the activity coefficients of the components in the

liquid phase. As mentioned, the ELECNRTL thermodynamic package that is an example of this approach, embedded in ASPEN PLUS software, was studied according to the purposes of this investigation. In this thermodynamic package, the Redlich-Kwong equation of state (RK) was selected to calculate the fugacity coefficient of components in the vapor phase.

But what has distinguished this thermodynamic package compared to other similar types, is the use of modified Electrolyte NRTL model to calculate the activity coefficients of the components in the liquid phase. The model proposed by Chen et al. [11], introduces the amount of excess Gibbs energy of the components in non-ideal electrolyte solutions, including two main parts that one is related to the local molecules and ions interactions (LI), and the other is related to Long-Range Ion-Ion Interaction (LR). It should be noted that in predicting the equilibrium behavior of electrolyte solutions, determining the ionic components amounts is of great importance, which is usually done by defining ionization reactions with inclusion of synthetic data or equilibrium constants. Kinetic and equilibrium data of these reactions are presented in [12].

In ASPEN PLUS software, several databases are available for thermodynamic calculations, which provide the possibility of using a different set of interaction parameters of ELECNRTL model and Henry constants. Among them, three special packages, namely as KEMDEA (Kinetic Equilibrium MDEA), KMDEA (Kinetic MDEA) and PMDEA (Posey MDEA) were imbedded that each would be used tailored to a specific usage and given the limits of experimental conditions for MDEA solutions. The calculation basis of components activity coefficients in the liquid phase is the Electrolyte NRTL model for all the packages which their interaction parameters have been recalled from different databases. The main difference between the KMDEA and KEMDEA packages is in the equation of state used for gas phase, so that the RK equation of state was used in the KEMDEA model, while the SYSOP15M equation of state was used in the KMDEA model. The PMDEA model developed based on the results of Posey et al. (1997) studies has considered two parameters of PH and electrical conductivity coefficient of the solution in estimating Henry constant parameters in order to eliminate measurement error of acid gases solubility, especially at low solubility rates [13]. Since the poor solubility changes can cause significant changes in PH and the value of solution electrical conductivity, thus, less error would occur in the measurement values. Finally, by including the PH and electrical conductivity, Posey and Rochelle provided new parameters for the calculation of Henry constants. In this study, three ELECNRTL thermodynamic packages of ASPEN PLUS software, name as KEMDEA, GLOBAL and PMDEA are selected for comparison. It should be noted that the GLOBAL database includes default values of the software.

The accuracy of estimation of mole fraction of molecular and ionic components considered in the equations in activity models are based on the accuracy of kinetic data and equilibrium constants of the existing chemical reactions. The ASPEN PLUS software package uses several reactions for ionization of acidic components and amine solutions that is presented in [12].

B. ACID GAS Thermodynamic Package

This package imbedded in ASPEN HYSYS for prediction of electrolyte solutions equilibrium behavior. This package has used the Electrolyte NRTL model to calculate the activity coefficients of the components in the liquid phase and the Peng-Robinson equation of state to calculate the vapor phase fugacity coefficient. The mentioned thermodynamic package have been developed merely for simulating the natural gas sweetening processes. In this thermodynamic package, according to recent studies, the possibility of using and examining the mixed amines has been also provided, and the relevant parameters have been calculated for each compound separately (Such as MDEA- PZ, Sulfolane-DIPA and MDEA-Sulfolane). The most important difference between ACID GAS thermodynamic package and the ELECNRTL package of ASPEN PLUS is in the set of interaction parameters used for each pair of molecules and ions.

3. RESULT AND DISCUSSION

A wide range of experimental data is needed to support validation of thermodynamic packages (ACID GAS, ELECNRTL). Since 1930 a large number of experimental solubility data for H_2S and CO_2 in aqueous amine has been published and presented by several investigators. Table 1 gives and overview on the previous results for these gases solubility in MDEA solution which are used for validating the selected thermodynamic packages. Where PH_2S and PCO_2 are the partial pressures of H_2S and CO_2, respectively.

A. Acid gas Solubility in MDEA Solutions

In this section, the simulation results of an acid gas-MDEA equilibrium stage (flash drum) by mentioned packages included in the ASPEN PLUS (KEMDEA, PMDEA, and GLOBAL MDEA) and ASPEN HYSYS (ACID GAS) which compared with experimental data are shown in Figures 1 to 10. The Average Absolute Deviation (AAD) for each thermodynamic package is also shown in Table 2.

A.1. Individual Acid Gas Solubility in Aqueous MDEA

Evaluation the solubility of CO_2 in the MDEA solution in absence of H_2S shows that the special data package of PMDEA compared to other ASPEN PLUS packages has a better estimation capability. However, the ACID GAS package predicts the CO_2 solubility as well as PMDEA (Figure 1).

The results of H_2S solubility in MDEA solution in absence of CO_2 indicate the lower accuracy of ACID GAS package compared to other packages. Assessment of results in Figure 2 shows that the error has occurred in high acid gas solubility. But in the low range of solubility, the results obtained from the thermodynamic ACID GAS package have enough accuracy.

A.2. Solubility of CO_2 and H_2S Simultaneously in Aqueous MDEA Solutions

Since in sweetening processes, both H_2S and CO_2 are usually present in the sour gas stream, thus, investigating the estimating ability of their interaction effect on solubility by thermodynamic packages is of utmost importance.

The results presented in Figures 3 to 10 demonstrate the ability to predict the H_2S and CO_2 solubility by ACID GAS package in low acid gases loading values. However, increasing this parameter (loading) will reduce the accuracy of solubility predicting by ACID GAS package compared to others. Also, this investigation shows that with increasing the mole fraction of CO_2 in sour gas (0.02-0.98), the results of PMDEA, KEMDEA and GLOBAL-MDEA packages will be partially better than ACID GAS package.

Table1. Literature data of acid gases solubility in aqueous MDEA solutions which are used in this paper for validating thermodynamic packages

Ref	Amine Concentration (wt. %)	Total Pressure (kPa)	Temp. (K)	P_{CO2} (kPa)	P_{H2S} (kPa)	Data NO.
[14]	MDEA (25.73%)	546.08-4386.8	313.17	533.9-4369.7	-	7
[15]	MDEA (46.78%)	6.21-1040.0	313.16	-	0-1000	13
[16]	MDEA (50%)	518-1999	323.15	10-1153	6-680	18
[17]	MDEA (50%)	200-8800	313.15	0.08-8120	0.295-2390	11
[18]	MDEA (35%) MDEA (50%)	690-7010 690-6990	298.15 298.15	0.3-10.12 0.62-14.9	0.19-15.2 0.19-11.3	18 18
[19]	MDEA+PZ (24, 0.08%) MDEA+PZ (24, 0.08%)	- -	313.15 333.15	0.10-95.3 0.08-83.1	- -	4 5
[20]	MDEA+PZ (47, 5 %) MDEA+PZ (47, 5 %)	- -	313.15 343.15	0.03-7.48 0.03-3.60	- -	4 3

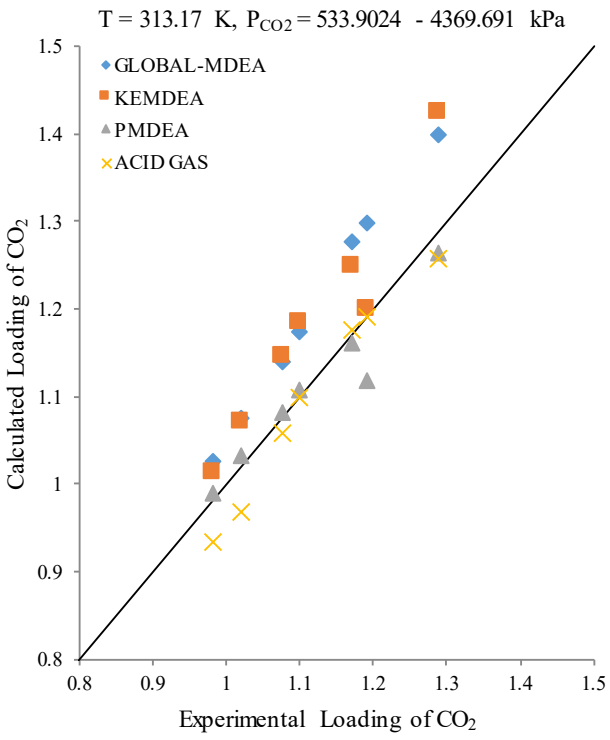

Figure 1. CO_2 solubility in MDEA (25.73wt.%)/CO_2 mixture at 313.17K [14]

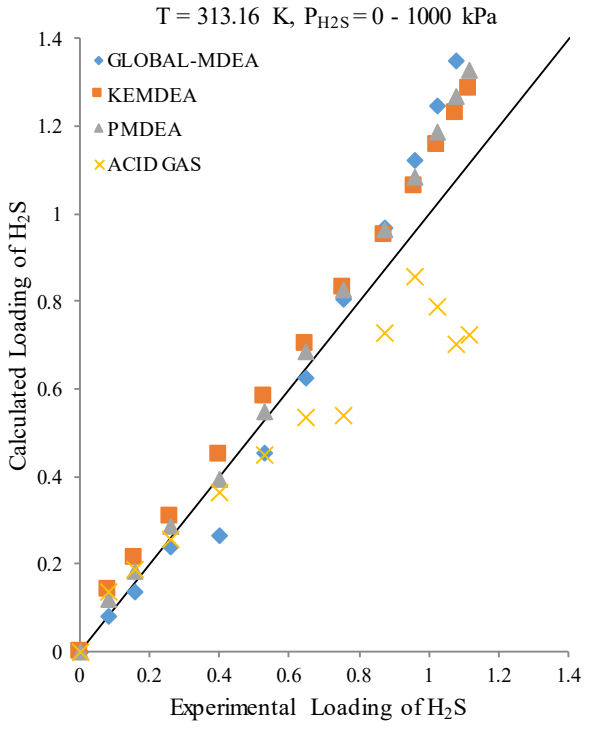

Figure 2. H_2S solubility in MDEA (46.78wt.%)/CO_2 mixture at 313.16K [15]

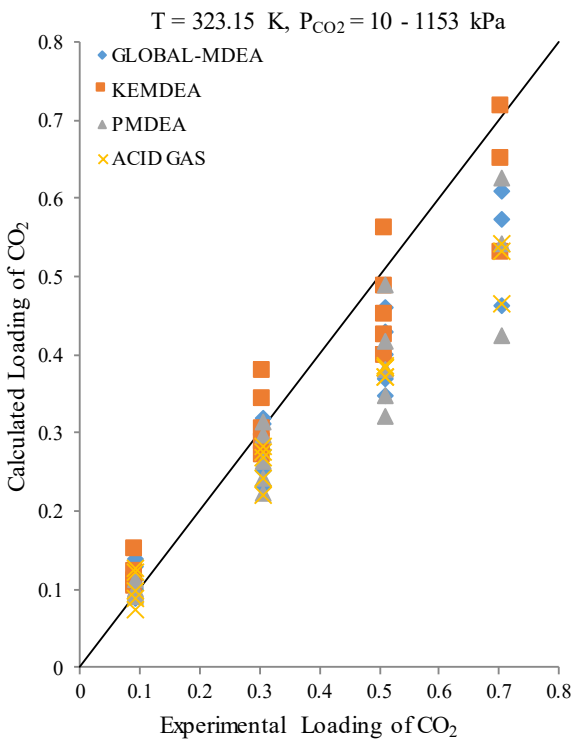

Figure 3. CO_2 solubility in MDEA (50 wt. %)/H_2S/CO_2 mixture at 323.15K [16]

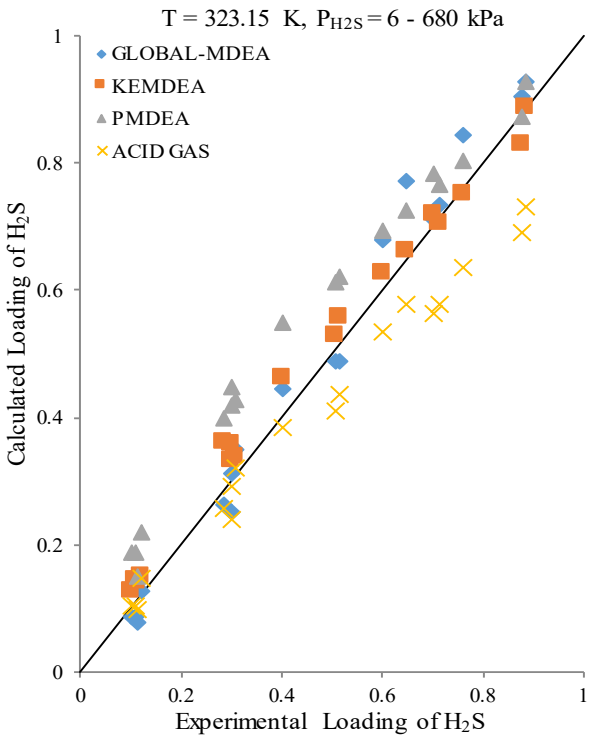

Figure 4. H_2S solubility in of MDEA (50 wt. %)/H_2S/CO_2 mixture at 323.15K [16]

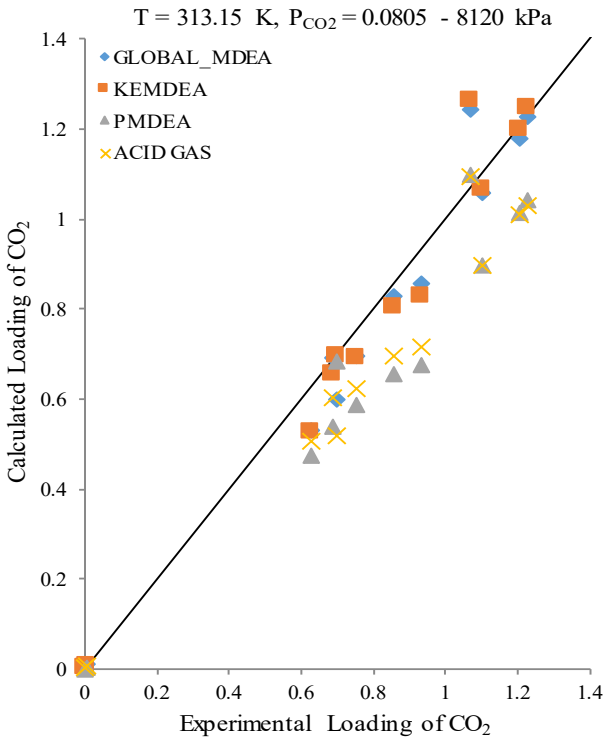

Figure 5. CO_2 solubility in MDEA (50 wt. %)/H_2S/CO_2 mixture at 313.15K [17]

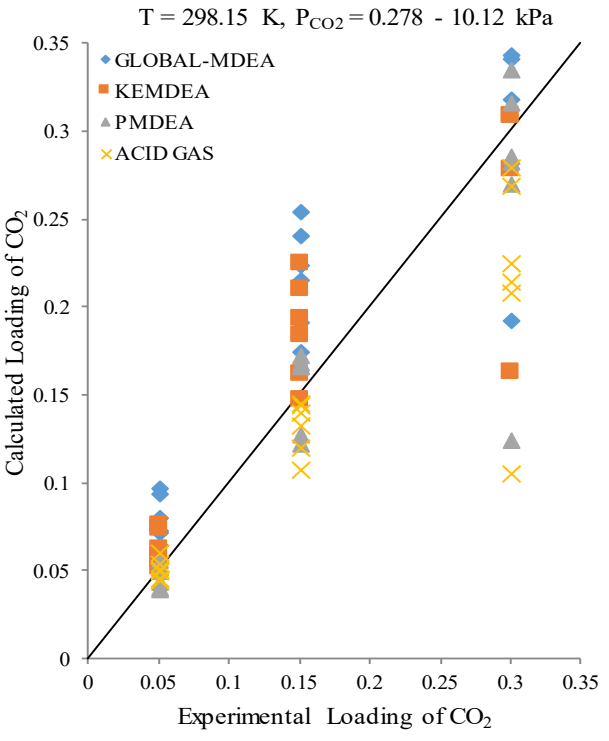

Figure 7. CO_2 solubility in MDEA (35wt.%)/H_2S/CO_2 mixture at 298.15K [18]

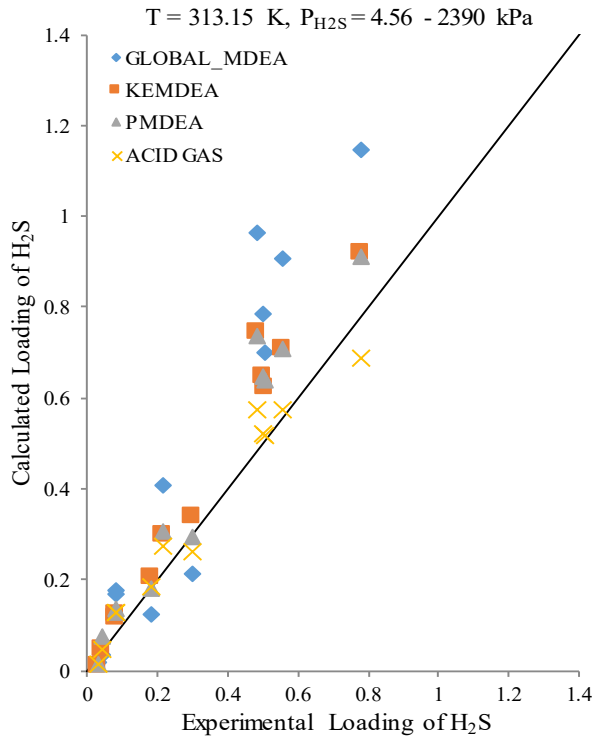

Figure 6. H_2S solubility in of MDEA (50 wt. %)/H_2S/CO_2 mixture at 313.15K [17]

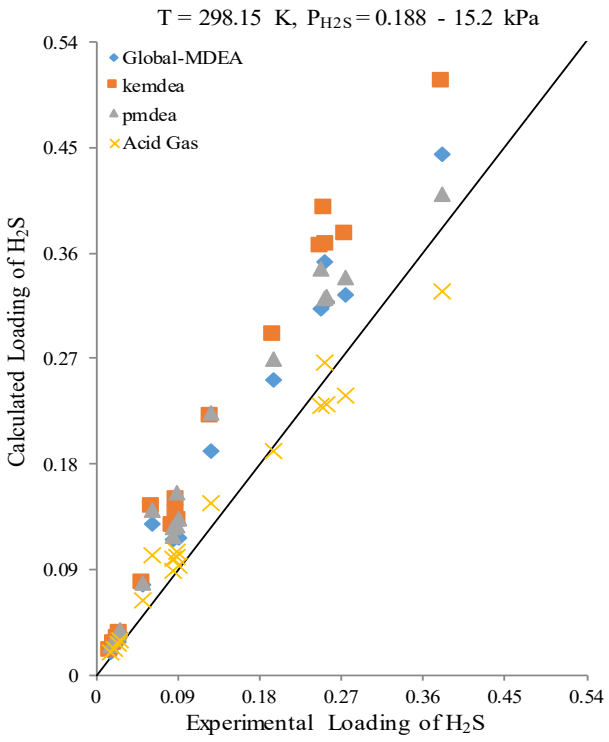

Figure 8. H_2S solubility in of MDEA (35wt.%)/H_2S/CO_2 mixture at 298.15K [18]

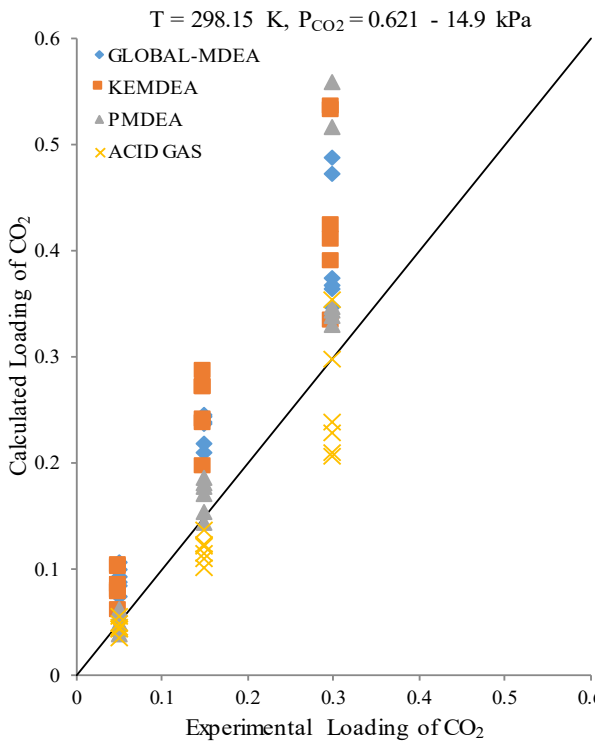

Figure 9. CO_2 solubility in MDEA (50wt.%) / H_2S/CO_2 mixture at 298.15K [18]

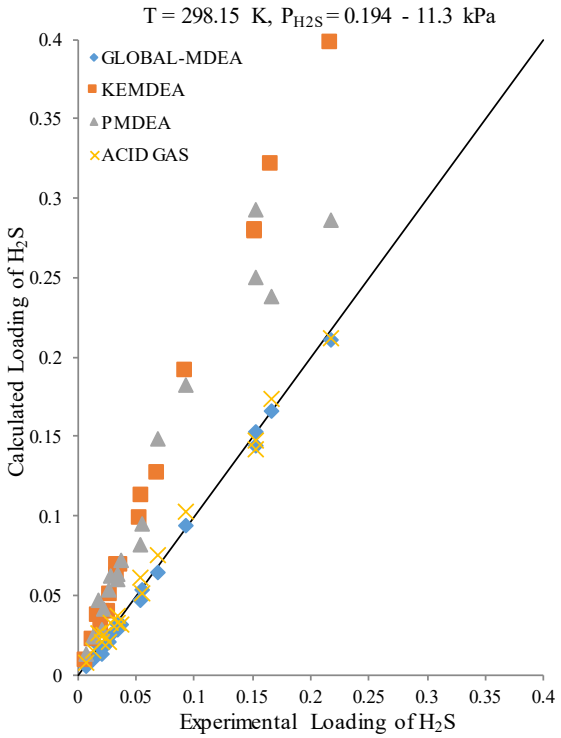

Figure 10. H_2S solubility in of MDEA (50wt.%)/H_2S/CO_2 mixture at 298.15K [18]

B. CO_2 Solubility in MDEA/PZ Solutions

In this section, the simulation results of an acid gas-MDEA/PZ equilibrium stage (flash drum) by GLOBAL MDEA/PZ (ASPEN PLUS) and ACID GAS (ASPEN HYSYS) which compared with experimental data are shown in Figures 11 to 14. The Average Absolute Deviation (AAD) for each thermodynamic package is also shown in Table 2.

The results shown in Figures 11 and 12, suggests the weakness of ACID GAS package in predicting of CO_2 solubility in activated amine solution. It is important to notice that, in Figures 11 and 12, the mass fraction of Piperazine in the solution is less than 1%, while industrial reports indicate that the mass fraction of Piperazine in gas sweetening processes is between 3% and 7%. According to the ASPEN TECH Company's claim regarding the enhancement of the ACID GAS thermodynamic package, a collection of experimental points based on gas processing operational data were used to tuning the ACID GAS package [10].

The results shown in Figures 13 and 14 indicate that by increasing the Piperazine concentration to 5 weight percent (gas processing operational range) the accuracy of CO_2 solubility prediction by ACID GAS package is also increased. However, the estimation capability of CO_2 solubility by ASPEN PLUS thermodynamic packages greatly reduced with increasing concentration of Piperazine more than 1 percent.

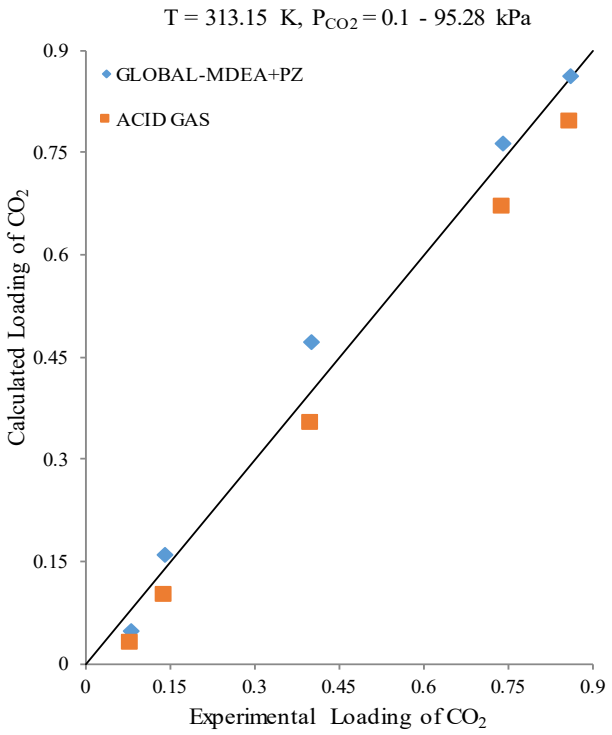

Figure 11. CO_2 solubility in of MDEA (24wt.%)/PZ (0.08wt.%)/CO_2 mixture at 313.15K [19]

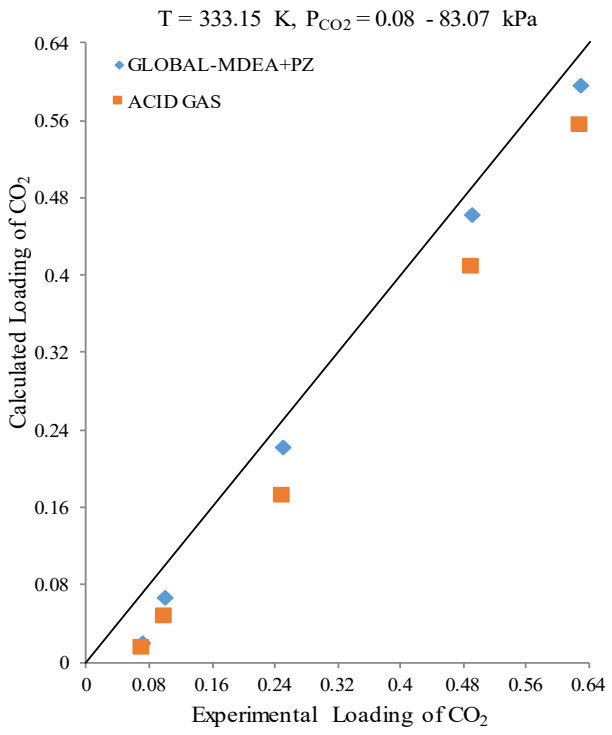

Figure 12. CO_2 solubility in of MDEA (24wt.%)/PZ (0.08wt.%)/CO_2 mixture at 333.15K [19]

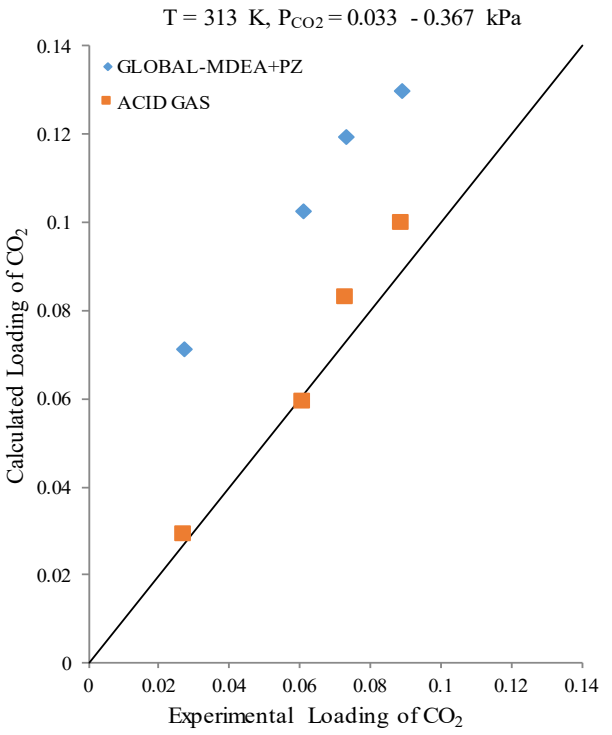

Figure 13. CO_2 solubility in of MDEA (47wt.%)/PZ (5wt.%)/CO_2 mixture at 313.15K [20]

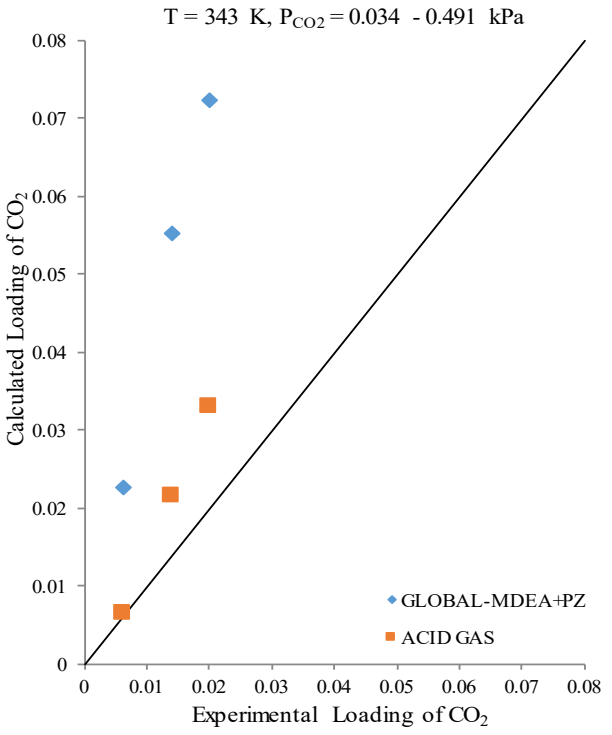

Figure 14. CO_2 solubility in of MDEA (47wt.%)/PZ (5wt.%)/CO_2 mixture at 343.15K [20]

Table 2. The Average Absolute Deviation of ELECNRTL and ACID GAS models in comparison with experimental data

Reference of experimental data	Figure	Model	(AAD) H_2S loading	(AAD) CO_2 loading
[14]	1	GLOBAL MDEA KEMDEA PMDEA ACID GAS	---- ---- ---- ----	7.1 5.8 1.8 2.4
[15]	2	GLOBAL MDEA KEMDEA PMDEA ACID GAS	15.5 18.9 13.9 22.2	---- ---- ---- ----
[16]	3	GLOBAL MDEA KEMDEA PMDEA ACID GAS	10.5 12.7 32.7 12.8	---- ---- ---- ----
[16]	4	GLOBAL MDEA KEMDEA PMDEA ACID GAS	---- ---- ---- ----	19.3 15.9 16.4 21.6
[17]	5	GLOBAL MDEA KEMDEA PMDEA ACID GAS	61.0 32.9 38.8 23.0	---- ---- ---- ----
[17]	6	GLOBAL MDEA KEMDEA PMDEA ACID GAS	---- ---- ---- ----	16.5 9.2 15.6 22.7
[18]	7	GLOBAL MDEA KEMDEA PMDEA ACID GAS	37.1 52.8 49.5 15.3	---- ---- ---- ----
[18]	8	GLOBAL MDEA KEMDEA PMDEA ACID GAS	---- ---- ---- ----	42.6 23.1 13.8 16.2
[18]	9	GLOBAL MDEA KEMDEA PMDEA ACID GAS	14.2 75.6 78.9 10.3	---- ---- ---- ----
[18]	10	GLOBAL MDEA KEMDEA PMDEA ACID GAS	---- ---- ---- ----	56.9 60.1 20.9 18.3
[19]	11	GLOBAL MDEA+PZ ACID GAS	---- ---- ---- ----	24.0 34.1
[19]	12	GLOBAL MDEA+PZ ACID GAS	---- ----	22.5 34.5
[20]	13	GLOBAL MDEA+PZ ACID GAS	---- ----	84.9 8.9
[20]	14	GLOBAL MDEA+PZ ACID GAS	---- ----	277.3 41.9

4. CONCLUSION

In this study, the prediction accuracy of H_2S and CO_2 solubility in aqueous MDEA and MDEA/PZ solutions has been investigated by using of two different packages of ASPEN PLUS and ASPEN HYSYS softwares (ELECNRTL and ACID GAS). The results showed that using of ACID GAS thermodynamic package has more accuracy specially for predicting the solubility of acid gases (at low concentration range) in MDEA solution, while, increasing the acid gas loading (specially CO_2 loading) will reduce the accuracy of solubility modeling by ACID GAS package compared to PMDEA, KEMDEA and GLOBAL-MDEA packages. The results also show that CO_2 solubility prediction by ACID GAS package is more accurate compared to GLOBAL-MDEA/PZ package when the Piperazine concentration is in the operational range of gas sweetening processes (3 to 7 wt. %).

ACKNOWLEDGMENT

This project was carried out within the research stream on optimization studies of BIDBOLAND gas refinery. The authors wish to thanks the refinery research unit officials for their valuable contributions, financial support of this research project and providing all necessary operating information.

REFERENCES

1. R. Deshmukh, A. E. Mather, "A mathematical model for equilibrium solubility of hydrogen sulfide and carbon dioxide in aqueous alkanolamine solutions," Journal of Chemical Engineering Science, Vol. 36, pp. 355-362, 1981.

2. M. Posey, K. G. Tapperson, G. T. Rochelle, "A simple model for prediction of acid gas solubilities in alkanolamines," Journal of Gas Separation and Purification, Vol. 1, pp. 181-186, 1996.

3. P. Patil, Z. Malik, M. Jobson, "Prediction of CO_2 and H_2S Solubility in aqueous MDEA solutions using an extended Kent and Eisenberg model," Institution of Chemical Engineers Symposium Series, Vol. 152, pp. 498-510, 2006.

4. P. Huttenhuis, N. J. Agrawal, G. F. Versteeg, "Solubility of Carbon Dioxide and Hydrogen Sulfide in Aqueous N-Methyldiethanolamine Solutions," Journal of Industrial and Engineering Chemistry, Vol. 48, pp. 4051-4059, 2009.

5. Y. Zhang, H. Que, C. C. Chen, "Thermodynamic modelling for CO_2 absorption in Aqueous MEA Solution with electrolyte NRTL model," Journal of Fuel and Energy Abstracts, Vol. 311, pp. 67-75, 2011.

6. Y. Zhang, C .C. Chen, "Thermodynamic modelling for CO_2 absorption in Aqueous MDEA Solution with electrolyte NRTL model," Journal of Industrial and Engineering Chemistry, Vol. 50, pp. 163-175, 2011.

7. E. Hansen, "Aspen HYSYS and Aspen Plus simulation programs for CO_2 absorption," Master's thesis, Telemark University College, Faculty of Technology, 2011.

8. L. E. Øi, "Removal of CO_2 from exhaust gas," M. C. Melaaen, revision of Ph.D. Dissertation Telemark University College Faculty of Technolo at porsgrumm, Norway, 2012.

9. L. E. Øi, "Comparison of Aspen HYSYS and Aspen Plus simulation of CO_2 absorption into MEA from atmospheric gas," Journal of Energy procedia, Vol. 23, pp. 360-369, 2012.

10. Optimize the entire gas process with acid gas cleaning. Available at: http://www. Aspentech .com/ products/V8-releash-prior, August 2013.

11. C .C. Chen, H. I. Britt, J. F. Boston, L. B. Evans, "Local composition model for excess Gibbs energy of electrolyte systems," AIChE Journal, Vol. 28, pp. 588, 1982.

12. ASPEN Physical Property system, Physical Property Methods and Models, chap.11.1.

13. M. L. Posey, G. T. Rochelle, "A Thermodynamic Model of Methyldiethanolamine-CO_2-H_2S-Water," Industrial & Engineering Chemistry Research, Vol. 36, pp. 3944-3953, 1997.

14. R. S. Boumedine, S. Horstmann, K. Fischer, E. Provost, W. Furst, J. Gmehling, "Experimental determination of carbon dioxide solubility data in aqueous alkanolamine solutions," Fluid Phase Equilibria, Vol. 218, pp. 85-94, 2004.

15. R. S. Boumedine, S. Horstmann, K. Fischer, E. Provost, W. Furst, J. Gmehling, "Experimental determination of hydrogen sulfide solubility data in aqueous alkanolamine solutions," Fluid Phase Equilibria, Vol. 218, pp. 149-155, 2004.

16. M. Dicko, C. Coquelet, C. Jarne, S. Northrop, D. Richon, "Acid gases partial pressures above a 50 wt% aqueous methyldiethanolamine solution: Experimental work and modelling," Fluid Phase Equilibria, Vol. 289, pp. 99-109, 2010.

17. F. Y. Jou, F. Otto, A. Mather, "The solubility of mixtures of H_2S and CO_2 in an MDEA solution," The Canadian Journal of Chemical Engineering, Vol. 75, pp. 1138-1141, 1997.

18. P. Huttenhuis, N. J. Agrawal, G. F. Versteeg, "Solubility of carbon dioxide and hydrogen sulfide in aqueous N-methyldiethanolamine solutions," Industrial & Engineering Chemistry Research, Vol. 48, pp. 4051-4059, 2009.

19. B. S. Ali, M. K. Aroua, "Effect of piperazine on CO_2 loading in aqueous solutions of MDEA at low pressure," International Journal of Thermophysics, Vol. 25, pp. 1863-1870, 2004.

20. S. Bishnoi, G. T. Rochelle, "Thermodynamics of piperazine/methyldiethanolamine/water/carbon dioxide," Industrial & Engineering Chemistry Research, Vol. 41, pp. 604-612, 2002.

پیش‌بینی حلالیت گازهای H_2S و CO_2 در محلول‌های MDEA و MDEA/PZ توسط بسته‌های ترمودینامیکی ACID GAS و ELECNRTL

- امید صباغ – میثم وحیدی فردوسی – محمد علی فنائی*

گروه مهندسی شیمی، دانشگاه فردوسی مشهد، مشهد، ایران

(ایمیل نویسنده مسئول: fanaei@um.ac.ir)

چکیـــــــده

در این مطالعه، میزان حلالیت گازهای اسیدی سولفید هیدروژن و دی‌اکسیدکربن در محلول‌های آبی MDEA و MDEA/PZ توسط بسته‌های مختلف ترمودینامیکی مورد ارزیابی قرار گرفته است. مقایسه نتایج مدل‌سازی با مجموعه‌ای از اطلاعات صنعتی و آزمایشگاهی که از سال ۱۹۹۷ تا ۲۰۱۰ منتشر گردیده، نشان از دقت بالای پیش‌بینی حلالیت گازهای اسیدی در محلول‌های مذکور با بسته ترمودینامیکی ACID GAS (نرم‌افزار اسپن هایسیس ۸/۳) در مقایسه با بسته ترمودینامیکی ELECNRTL (نرم‌افزار اسپن پلاس ۸/۲) بویژه در محدوده غلظت‌های عملیاتی واحدهای شیرین سازی گاز طبیعی دارد.

واژگان کلیدی: MDEA، PZ، بسته ترمودینامیکی، حلالیت گازهای اسیدی، ACID GAS، ELECNRTL.