1. INTRODUCTION

The removal of CO$_2$ and H$_2$S from the flue gas is essential in the process of natural gas purification. In addition, for the design and construction of gas transport equipment, experimental data on the solubility of CO$_2$ and H$_2$S in aquatic alkanolamines are required [1]. Due to the weakness or power of various alkanolamines in absorption of various acid gases, the choice of a suitable combination of these materials in the process of natural gas purification has been studied [2-4]. Also, at a wide range of temperatures and pressures, various experiments are carried out to obtain a suitable thermodynamic model for desired estimation of experimental data [5-7]. It became clear that, because of the ionization of these mixtures, the models that utilize the activity coefficient have been used extensively in research projects [8-10]. Typically, in these models, various equations have been used to predict wide-range of interactions using the Pitzer-Debye-Huckel method and narrow-range of interactions using other types of methods [11-13].

Separation factor is an important feature in the choice of alkanolamine solution to eliminate acidic gas or to interpret the kinetic mechanism of acidic absorption in alkanolamine solution. Recently, Barzagli et al. [14] have studied CO$_2$ absorption and desorption experiments with alkanolamine mixtures in non-aqueous solvents (ethylene glycol mixtures and 2,1 propanediol with methanol or ethanol) [13]. They reported relatively low separation temperature (about 80°C) and less...
evaporation. They have shown that amine recovery in non-aqueous solvents can be easily done [6]. The results of their study are given with the average and maximum relative deviation between experimental data and linear matching values. These numbers provide information about the linear extrapolation. Also, the decrease in the strength of the protonated alkanolamines was observed with an increase in fractions of organic composition and temperature. The greatest effect is observed for butanol-water mixtures as solvent. This result was expected since the butanol-water solvents had the lowest dielectric values compared to sulfolane-water and methanol-water solvents.

In the case of acid gases, thermodynamic modeling of the equilibrium solubility is also an important topic for the design of gas purification and CO₂ capture processes. Zoghi and Feizi [15] calculated the solubility of CO₂ in aqueous solutions of 2, 2-aminoethyll amino ethanol (AEEA) and compare the results with the Deshmuch-Mather model. Finally, for the quaternary system water-CO₂-N-methyldiethanolamine (MDEA)-AEEA, the modified Peng-Robinson cube parameters which were modified by the electrolyte are correlated with the emPR-CPA equation of state (EoS) and finally, the solubility of CO₂ is calculated. They studied equilibrium solubility of CO₂ in the mentioned solution in the range of 308.2 to 368.2 K and the 101 to 4448 kPa [9].

2. THERMODYNAMIC MODELING

In this work, we have used gamma-phi (γ-φ) method for modeling the behavior of under investigation systems. Specifically, to calculate the activity coefficients of the components in the gas phase, the N-Wilson-NRF state equation and to calculate the fugacity coefficients in the liquid phase, the Peng Robinson equation has been used [16]. Using the qualitative properties (PVT), we can calculate all thermodynamic properties and thermodynamic potential energies. Here, we will investigate the behavior of PVT of a pure substance in gas and liquid states.

Parameters (a and b) which are called gravity and repulsion parameters, respectively. Here, k₁ and k₂ are numerical constants that obtained by the critical properties for each pure substance.

Peng-Robinson presented his equation as follows Equation (2) where k₁=2 and k₂=-1 [17]:

\[
P = \frac{RT}{v-b} - \frac{a(T, \omega)}{v(v+b)+b(v-b)}
\]

In this equation, a, b are:

\[
a = 0.457235 \frac{RT^2}{P_c}, \quad b = 0.077796 \frac{RT}{P_c}
\]

The k equation is obtained by fitting steam pressure data from boiling point to critical point in Equation (2):

\[
k = 0.37464 + 1.54226\omega - 0.26993\omega^2
\]

The cubic equations of state for the blends are written as follows in Equation (3):

\[
P = \frac{RT}{v-b} - \frac{a(T, \omega)}{v^2 + k_1b + k_2b^2}
\]

Also, \( \Phi \) is the molar volume of the mixture. In this case, using the mixing rule, the values of a and b can be set according to the aᵢ and bᵢ parameters for the pure substance.

2. 1. Mixture Fugacity Coefficient Using Peng-Robinson Equation

The Peng-Robinson equation of state can be divided as follows in Equation (4) [8-9]:

\[
P = \frac{RT}{v-b} - \frac{a(z, \omega)}{(v + (1 + \sqrt{2})b)(v + (1 - \sqrt{2})b)}
\]

By proper derivation from Equation (2), the fugacity coefficient of component i is obtained as follows in Equation (5):

\[
\ln \phi_i = \frac{b_i}{e_i(z - 1)} - \ln(z - 1) - \ln(z - 2) - A_i \frac{z^{\alpha_i}}{2\sqrt{2}B} \frac{b_i}{e_i} \ln \left( \frac{z + B(1 + \sqrt{2})}{z + B(1 - \sqrt{2})} \right)
\]

2. 2. An Integral Method for the Calculations of Vapor-liquid Equilibrium

In the integral method, the equation of fugacity is used directly for equilibrium calculations. Therefore, for the equilibrium of two phases of vapor and liquid, the equation of fugacity is used based on the following Equation (6) [18, 19]:

\[
f_i^V = f_i^L
\]

In this case, the following two methods are proposed for the calculations of vapor-liquid equilibrium, each method depending on the nature of the components:

I. The equation of state approach (φ-φ Approach)
II. The activity coefficient approach (γ-φ Approach)

In the equation of state approach, the fugacity of each component in the vapor and liquid phases is written as follows:

\[
f_i^V = y_i \phi_i^V P \text{ for vapor and } f_i^L = x_i \phi_i^L P \text{ for liquid and } x_i, y_i \text{ are the molar fractions of component } i \text{ in liquid and vapor phases, respectively. Hence Equation (7):}
\]

\[
K_i = \frac{y_i}{x_i} = \frac{\phi_i^V}{\phi_i^L}
\]
where $K_i$ is the ratio of components (K-value) for component $i$. Therefore, with the proper equation of state, the coefficients of fugacity can be calculated.

The activity coefficient is the quantity that represents the deviation of the non-ideal behavior of liquid mixtures from the ideal behavior of Lewis-Randall. When we have an ideal solution, the activity coefficient is 1 and the fugacity of component $i$ is ideally written as follows in Equation (8):

$$f_i^{id} = x_i f_{i, pure}$$

(8)

In other words, liquid solutions can be divided into (ideal dilution solution) and (non-ideal solution). Therefore, in order to calculate the activity coefficients, it is necessary to calculate the first fugacity from the pure material. Therefore, fugacity can be achieved by using a dense phase fugacity in Equation (9):

$$f_{i, pure} = P_i^{out} q_i^{out} \exp\left(\frac{\mu_i(P-P_i^{out})}{RT}\right)$$

(9)

The saturation fugacity coefficient ($q_i^{out}$) is obtained at a saturation point at temperature $T$, which can be calculated using the ratio of the fugacity coefficient for the pure component.

2. 3. Activity Coefficient in Liquid Solutions

For liquid solutions, the activity coefficient is used as the standard deviation from the ideal state, so for the component in liquid solution and constant temperature it can be written as Equation (10) [20-22]:

$$\gamma_{i, 0} = \frac{f_i(T, P, x_i)}{f_i^{LR}(T, P)} = \frac{f_i(T, P, x_i)}{x_i f_i^{0}(T, P)}$$

(10)

The Lewis-Randall activity coefficient is used for the solutions in which the components are either dissolved or convergent, in any ratio from dilute to concentrated. On the other hand, some solutions have a positive deviation ($\gamma_i > 1$) from the Lewis-Randall law, and others have negative deviations ($\gamma_i < 1$). For some solutions, you cannot use the Lewis-Randall activity factor. In this kind of systems, components are not resolved in each other with any ratio. In this case, it is not possible to use the Lewis-Randall activity factor for vapor in the solution. In this case, pure vapor may not be available as a standard solution at system temperature and pressure. Another example is the solubility of electrolytes and polymers in solvents. In this case, the activity coefficient for component $i$ is defined as Equation (11):

$$\gamma_i = \frac{f_i(T, P, x_i)}{x_i H_i(T, P)}$$

(11)

Thus, for equilibrium calculations in liquid and solid phases, using the gamma-phi method, we need to have a proper function for calculating the activity coefficient of the components in the solution. On the other hand, we know that in order to obtain an appropriate model of the activity coefficient, the Gibbs energy function ($G^f$) is necessary for the solution which is shown in Equation (12).

$$\ln \gamma_i = \left(\frac{\partial (G^f_i/RT)}{\partial N_i}\right)_{r, s, \mu} = \left(\frac{\partial (N_i G^f_i/RT)}{\partial N_i}\right)_{r, s, \mu}$$

(12)

2. 4. Local Composition Models

The local composition model is a semi-experimental method that derives from the concept of the local composition of molecules in a network. The local composition concept was first introduced by Wilson in 1964 [23].

In 2009, the Haghitalab and Mazzolani present new N-Wilson-NRF model which provided a random mode for each cell based on the literature stated [24]. Local molecular fractions are defined using non-random $\Gamma_{ij}$ coefficients Equation (13):

$$x_{ij} - x_i, \Gamma_j - \Gamma_j = \frac{\beta_i}{\sum \beta_i}$$

$$\Gamma_i = \Gamma_i / \beta_i$$

(13)

While $\beta_i \neq \beta_j$, $\beta_i = \beta_j = 1$ and $N$ is the number of components in the system and $Z$ is the coordination number. Using Equation (13), we can obtain the hypertensive enthalpy formula for a two-component mixture. Assuming that the temperature is independent of entropy Equation (14):

$$\frac{x_i H_i(T, P)}{RT} = Z[x_1 \ln \Gamma_{ij} + x_2 \ln \Gamma_{ji} + x_i x_j \ln (\beta_i \beta_j)]$$

(14)

by deriving the Equation (14), the activity coefficient for a component in a two-component mixture is obtained as Equation (15):

$$\ln \gamma_i = Z[1 + \ln \Gamma_i - x_i (\Gamma_i - \Gamma_j) + x_j x_i \ln (\beta_i \beta_j)]$$

(15)

The general format of the equations for a multi-component mixture is obtained as Equations (16) and (17):

$$\frac{g^E}{RT} = Z[\sum x_i (\ln \Gamma_i + \frac{\sum x_j \ln \beta_j})]$$

(16)

$$\ln \gamma_i = Z[1 + \ln \Gamma_i - \sum x_j (\Gamma_i - \ln \beta_j) + x_i x_j \ln (\beta_j)]$$

(17)

$$\lambda_y = (h_y - h_{\phi})/RT, \lambda_y = \lambda_y = 0, \beta_i = \beta_j = 1.0$$

2. 5. The Process Flowchart of Calculating CO2 Gas Solubility

The general method for calculating the
vapor pressure of each of the various system components using the bubble-pressure calculations flowchart is shown in Figure 1. For higher order systems, these equations for the mixtures can be used [17]. As shown in Figure 1 by the help of laboratory pressure, temperature and composition of the components percentage in the liquid phase, by the initial guess for the system pressure, the simulations can be done, and also the composition of the components in the gas phase and the calculated pressure can be gained using this system. It should be noted that for the two-component and multi-component systems the overall process is the same and for the higher order systems, the classic rules of the hybrid can be used.

3. RESULT AND DISCUSSION

3.1. Quaternary Water-CO$_2$-MDEA-2-2-Aminoethyl (amino) ethanol System

One of the most important factors in the design of absorption unit is the solvent material. The most important features of a solvent for absorption are higher absorption speed, better function in absorption process, high net recycling capacity and better chemical stability. In the previous studies [25], researchers measured the rate of CO$_2$ absorption among various amines, which showed that 2-2-Aminoethyl(Amino)Ethanol (AEEA) and (2-Aminoethyl) 1,3-Propandiamine solvents can absorb CO$_2$ more quickly. Ma’mum et al. [26] used a screening test and found that the aqueous solution of AEEA could be used as an absorber in the process of absorbing CO$_2$ from combustion gases. AEEA has a high absorption rate and net recycling capacity, which is clearly higher than monoethanolamine indexes. Also, this material has also shown its high absorption capacity at higher CO$_2$ loads. Recently, Zoghi et al. [27] investigated the effect of various activators in methyl diethanolamine on the CO$_2$ capture process. They showed that AEEA can greatly increase the rate of CO$_2$ absorption compared with other activators such as Piperazine. The amount of waste lost in the recovery process is another important factor that should be considered in choosing the appropriate solvent. Wilson [28] measured the vapor pressure of AEEA under the temperature of the recovery process (395 K) and showed that AEEA had much lower vapor pressure (959 Pa) than monoethanolamine (15900 Pa). Also, thermodynamic modeling of the equilibrium solubility of acid gases in the process of sweetening and absorbing CO$_2$ gas is another vital point. When acid gases are absorbed in an aqueous solution of alkanolamine, different ionic species are produced by chemical reactions. It makes it difficult to calculate the liquid-vapor balance for aqueous solutions of alkanolamine. In this section, we used the gamma-phi(γ-φ) method and the experimental data of Zoghi experiment [15], to develop a thermodynamically model of the quaternary water-CO$_2$-MDEA-AEEA system. It is important to assume the system physically, in order to reduce the volume of the calculations and to simplify the process of chemical reactions. Based on the results of the above four-component system, the target function was equal to 19,537.

| TABLE 1. Optimized Values of the N-Wilson-NRF Equation for the Quaternary Water-CO$_2$-MDEA-AEEA System |
|-------------------------------------------------|
| i-j | $\lambda_{ij}$ | $a_{ij}$ | $b_{ij}$ |
|-----|----------------|---------|---------|
| CO$_2$-AEEA | $\lambda_{14}$ | -27/8734 | -48669/667 |
| AEEA-CO$_2$ | $\lambda_{41}$ | -8/3472 | -7713/6611 |
| H$_2$O-AEEA | $\lambda_{24}$ | 279/2278 | -94/2250 |
| AEEA-H$_2$O | $\lambda_{42}$ | 8/4826 | 1323/4516 |
| MDEA_AEEA | $\lambda_{34}$ | 5/8430 | -62/8829 |
| AEEA_MDEA | $\lambda_{43}$ | 3/2783 | -221/7266 |

$\lambda_{ij} = a_{ij} + \frac{b_{ij}}{T}$
3. 2. Interaction Parameter  In the previous sections and in the equation of activity coefficients, we used equation 17 to calculate the interaction parameters, where two parameters a and b were obtained and optimized simultaneously. In this section, by developing the interaction parameter equation, we examined the effect of this change on the accuracy of the calculations.

The equation of interaction parameter with the three sub-parameters a, b and c is defined in Equation (18):

\[
\lambda_i = a_i + \frac{b_i}{T} + c_i \left( \frac{T}{T^0} - T^0 \right) + \ln \left( \frac{T}{T^0} \right)
\]  

(18)

For the quaternary water-CO\textsubscript{2}-MDEA-AEEA system, the target function was equal to 19.084 and the values of interaction parameters are shown in Table 3.

| Loading | P\text{exp}(kPa) | P\text{cal}(kPa) | Loading | P\text{exp}(kPa) | P\text{cal}(kPa) |
|---------|----------------|-----------------|---------|----------------|-----------------|
| 308.2(K)| 103.3          | 130.66          | 0.516   | 100.7          | 90.96           |
| 0.735   | 111.6          | 140.02          | 0.544   | 114.5          | 114.5           |
| 0.753   | 146.7          | 171.0261        | 0.56    | 128.3          | 129.3136        |
| 0.807   | 187.4          | 187.4           | 0.62    | 133.5          | 197.655         |
| 0.832   | 232.9          | 207.4161        | 0.652   | 163.9          | 242.6039        |
| 0.862   | 350.6          | 227.9479        | 0.704   | 249.7          | 329.7518        |
| 0.89    | 483.8          | 240.3064        | 0.765   | 373.8          | 456.6946        |
| 0.934   | 746.8          | 263.113         | 0.805   | 531.8          | 556.0085        |
| 0.944   | 908.8          | 271.57          | 0.846   | 793.2          | 672.2862        |
| 0.954   | 1082           | 280.1942        | 0.868   | 963.6          | 741.1162        |
| 0.966   | 1254.7         | 290.766         | 0.885   | 1165.9         | 797.5861        |
| 0.974   | 1438.8         | 298.3437        | 0.895   | 1335.3         | 832.1222        |
| 0.988   | 1652.1         | 311.357         | 0.917   | 1574.4         | 911.7242        |
| 1.002   | 1952.7         | 324.6064        | 0.934   | 1798.8         | 976.6611        |
| 343.2(K)| 170.9          | 158.3485        | 0.406   | 281            | 177.09          |
| 0.489   | 189.4          | 194.8241        | 0.429   | 322            | 224.31          |
| 0.514   | 230.9          | 267.88907       | 0.47    | 405.5          | 327.27          |
| 0.556   | 349.6          | 426.1947        | 0.527   | 585.6          | 514.45          |
| 0.626   | 468.8          | 609.5557        | 0.543   | 649.5          | 577             |
| 0.688   | 593.3          | 759.5985        | 0.589   | 821            | 783.34          |
| 0.73    | 724.3          | 876.4672        | 0.626   | 1010           | 979.8           |
| 0.759   | 968.3          | 1110.433        | 0.67    | 1241.7         | 1251.96         |
| 0.81    | 1172.2         | 1172.2          | 0.708   | 1490.3         | 1523.53         |
| 0.822   | 1316.5         | 1239.3          | 0.742   | 1656.7         | 1796.68         |
| 0.835   | 2128.4         | 1596.662        | 0.852   | 2758.1         | 2917.502        |
| 0.896   | 2373.6         | 1707.78         | 0.867   | 3002.9         | 3101.764        |
| 0.913   | 2898.6         | 1728.127        | 0.883   | 3266.8         | 3305.867        |
| 0.916   | 3082.6         | 1817.519        | 0.899   | 3502.9         | 3524.257        |
| 0.929   | 3253.2         | 1910.189        | 0.916   | 3869.6         | 3766.08         |
TABLE 3. Optimized Values of the N-Wilson-NRF Equation in the Quaternary Water-CO$_2$-MDEA-AEEA System

| i,j | $\lambda_{ij}$ | $a_{ij}$ | $b_{ij}$ | $c_{ij}$ |
|-----|----------------|-----------|-----------|-----------|
| CO$_2$-AEEA | $\lambda_{14}$ | -27/8734 | -48669/667 | -0/01153 |
| AEEA-CO$_2$ | $\lambda_{41}$ | -8/3472 | -7713/6611 | -0/01552 |
| H$_2$O-AEEA | $\lambda_{34}$ | 287/2285 | -941/2250 | -0/07370 |
| AEEA-H$_2$O | $\lambda_{42}$ | 8/4826 | 1323/4516 | -0/01154 |
| MDEA_AEEA | $\lambda_{34}$ | 5/8430 | -62/8829 | 0/01758 |
| AEEA_MDEA | $\lambda_{43}$ | 2/3283 | -221/7266 | 0/01680 |

Figure 2. Molecular Concentration of CO$_2$ in Aqueous Solution of MDEA+AEEA

4. CONCLUSION AND FUTURE PERSPECTIVE

In this project, the solubility of CO$_2$ gas was investigated in alkanolamine solutions. The N-Wilson-NRF model and the activity coefficient method ($\gamma$-Approach) were used to calculate solubility of CO$_2$. The two-component water-CO$_2$ model was modeled and the results were obtained by the accuracy of 1.38 of experimental results. In a three-component, water-CO$_2$-MDEA system with the amount of 6.913, the optimization was developed.

The quaternary water-CO$_2$-MDEA-AEEA system was optimized with an overall approximation of 19.537 for all experiment data. By changing the interaction parameter equation of $\lambda_{ij}$ to the three-parametric equation in the two-component system, the approximation of 6.581 and in the three-component system, 19.084 were obtained. The systems used in this study have made a completely reasonable approximation considering that the solubility modeling of gas in solutions is based on the physical interaction. To make the calculation and mentioned systems more accurate, some suggestions are presented which are:

1. considering chemical reactions in the liquid phase to improve the accuracy of the model,
2. performing more experiments at higher temperatures and pressures to obtain more operational data,
3. using mixing rules in multi-component system computing procedure,
4. using the equations of electrolyte activation to improve the accuracy of the model.

5. REFERENCES

1. Barzagli, F., Mani, F. and Peruzzini, M. "A comparative study of the CO$_2$ absorption in some solvent-free alkanolamines and in aqueous monoeiulanolamine (MEA)", *Environmental Science & Technology*, Vol. 50, No. 13, (2016), 7239-7246. DOI: 10.1021/acs.est.6b00150
2. Akhmetshina, A.I., Petukhov, A.N., Vorotyntsev, A.V., Nyuchev, A.V. and Vorotyntsev, I.V., "Absorption behavior of acid gases in protic ionic liquid/alkanolamine binary mixtures", *ACS Sustainable Chemistry & Engineering*, Vol. 5, No. 4, (2017), 3429-3437. DOI: 10.1021/acs suschirng.7b0092
3. Akbartabar, I., Yazdanshenas, M.E., Tayebi, H.-A. and Nasirzadeh, N., "Physical chemistry studies of acid dye removal from aqueous media by mesoporous nano composite: Adsorption isotherm, kinetic and thermodynamic studies", *Physical Chemistry Research*, Vol. 5, No. 4, (2017), 659-679. DOI: 10.22036/PCR.2017.83378.1371
4. Patel, H.A., Karadas, F., Canlier, A., Park, J., Deniz, E., Jung, Y., Attihan, M. and Yavuz, C.T., "High capacity carbon dioxide adsorption by inexpensive covalent organic polymers", *Journal of Materials Chemistry*, Vol. 22, No. 17, (2012), 8431-8437. https://doi.org/10.1039/C2JM30761H
5. He, X., Fu, C. and Hägg, M.-B., "Membrane system design and process feasibility analysis for CO$_2$ capture from flue gas with a fixed-site-carrier membrane", *Chemical Engineering Journal*, Vol. 268, (2015), 1-9. DOI: 10.1016/j.cej.2013.03.026
6. Yan, H., Fu, Q., Zhou, Y., Li, D. and Zhang, D., " CO$_2$ capture from dry flue gas by pressure vacuum swing adsorption: A systematic simulation and optimization", *International Journal of Greenhouse Gas Control*, Vol. 51, (2016), 1-10. https://doi.org/10.1016/j.ijggc.2016.04.005
7. Shi, W., Siefert, N.S. and Morreale, B.D., "Molecular simulations of CO$_2$, H$_2$, H$_2$O, and H$_2$S gas absorption into hydrophobic poly(dimethylsiloxane)(PDMS) solvent: Solubility and surface tension", *The Journal of Physical Chemistry C*, Vol. 119, No. 33, (2015), 19253-19265. DOI: 10.1021/acs.jpcc.5b05806
8. Saedeh, N., Stenby, E.H. and Thomsen, K., "Thermodynamic modeling of hydrogen sulfide absorption by aqueous n-methylatediolamine using the extended unipaque model", *Fluid Phase Equilibria*, Vol. 392, (2015), 24-32. https://doi.org/10.1016/j.fluid.2015.01.024
9. Barari-Harooni, A., Najafi-Marghmaleki, A. and Mohammadi, A.H., "Efficient estimation of acid gases (CO$_2$ and H$_2$S) absorption in ionic liquid", *International Journal of..."
چکیده
زیست‌های هیدروژن سولفید و دی‌آورده‌ای کربن از کار دوکلا در فرایند تعیین جای عصبی و گیراندازی گازهای اسیدی اهمیت دارد به مثالی برای طراحی و نهایت آب‌داری

یک ترکیب مناسب از این مواد در فرایند تصفیه گاز طبیعی مورد مطالعه قرار گرفته و در دما و فشارهای مختلف آزمایش و بررسی شده است. در این مقاله با مطالعه داده‌های آزمایشگاهی و محاسباتی مقایسه ای بین جهت‌های مختلف و مدل‌های تشکیل دهنده یونی این مخلوط‌ها و در نهایت بررسی دقیق‌تری را برای پیش‌بینی کربن‌های کربن‌داری و در حد گازی از روش میکرو‌کربن‌های کربن‌داری استفاده می‌کنند.

در مورد مدلهای شتاب‌دار نیز می‌تواند کاربردی به در نظر گرفته شود که به طور معمول این مدل‌ها برای پیش‌بینی قابلیت گازهای کربن‌داری و در نهایت بررسی دقیق‌تری را برای پیش‌بینی کربن‌های کربن‌داری استفاده کنند.

بر آنها در جهت انتخاب حلال و مدلهای تصفیه‌گذاری است.