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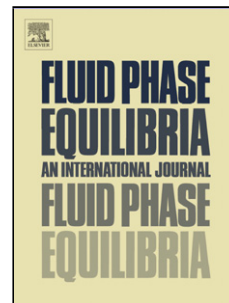
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measurement solubility of carbon dioxide + hydrogen sulfide into aqueous blends of alkanolamines at high pressure

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Abstract

Treatment of the sour natural gas is a major step in natural gas processing so that the acid gases such as H₂S and CO₂ are removed from natural gas stream. The acid gases are harmful to environment and destroy the production equipment so that their presence in gas stream leads to corrosion and lowering heating value. On the other hand, for reliable and optimum design of separation equipment, primarily sufficient and accurate equilibrium data of the acid gases solubility in the aqueous alkanolamines is required. In this work, the simultaneous solubility of the H₂S+CO₂ in the alkanolamine mixtures is measured at 343 K and total pressure range of 0.1-2.1 MPa. The blends are studied as the aqueous mixtures of N-methyldiethanolamine (MDEA)+2-amino-2-methyl-1-propanol (AMP)+Piperazine (Pz) and the aqueous mixtures of Diisopropanolamine (DIPA), AMP and Pz. For the acid gas solubility measurements, a high pressure static apparatus is used through a volumetric method. The mass fraction of the total alkanolamine is fixed at 0.45 and the results are presented as the partial pressure of each acid gas against its loading (mole acid gas / total mole amine) and mole fraction. The influence of the AMP and Pz on the aqueous DIPA-based and MDEA-based systems are studied so that it is observed that the absorption of the CO₂ in the aqueous alkanolamine enhances through separate blending of the AMP and Pz with the aqueous system of MDEA or DIPA and the absorption of the H₂S reduces in both of the aqueous DIPA-based and MDEA-based systems.

Keywords: Acid gas solubility, H₂S, CO₂, alkanolamine, piperazine.

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1. Introduction

The natural gas is contaminated with several impurities such as H_2S and CO_2 that forms an acidic solution in the presence of water. These acid gases should be removed from natural gas because they destroy process equipment and transportation lines; pollute the environment; and reduce heating value of natural gas. Moreover, H_2S is a poisonous and toxic gas so that both CO_2 and H_2S are corrosive and damage pipeline, valves, etc. [1]. To remove these gases from natural gas, several processes such as physical and chemical absorption are applied through using an acid gas removal unit which consists of a chemical or physical contactor and a stripper column. Using alkanolamines in a chemical absorption process presents some advantages such as high capacity for absorption, high reaction rate with H_2S and CO_2 , low vapor pressure, low cost and low corrosiveness [2, 3]. An alkanolamine molecule possesses at least one amino group and one hydroxyl group in which these groups intensify the alkalinity of the solution to improve absorption of the acid gases and reduce the vapor pressure of the solution [4]. The amines are classified in three types, namely primary, secondary and tertiary alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA) and N-methyldiethanolamine (MDEA). MEA and DEA form carbamate in reaction with CO_2 , because stability of carbamate is relatively high and presents a low rate of hydrolysis to bicarbonate so that the loading of CO_2 absorption is limited to about 0.5 mole of CO_2 per mole of amine [5]. Another secondary alkanolamine is diisopropanolamine (DIPA), which uses in the ADIP, Sulfinol and SCOT processes, that the selectivity of DIPA is more towards to H_2S than CO_2 . In addition, DIPA presents low regeneration steam requirements, great potential for absorption of the other sulfur compounds such as COS and CS_2 that it is less corrosive in comparison to the other primary or secondary alkanolamines [6]. MDEA is known more for its selective removal of H_2S in comparison to CO_2 , because MDEA doesn't form carbamate and presents a lower rate of reaction with CO_2 respect to primary and secondary alkanolamines [7] so that MDEA can absorb one mole CO_2 per mole of amine stoichiometry. The low enthalpy of the MDEA reaction with H_2S and CO_2 leads to lower energy requirement for the solvent regeneration that is another feature of MDEA [8]. Both DIPA and MDEA present fast reactivity with H_2S so that the protonation reaction can proceed immediately without controlling the reaction kinetically [9,10].

Another class of alkanolamines is sterically hindered amines such as AMP so that a sterically hindered amine is a primary alkanolamine structure in which amino group is attached to a ternary

carbon atom. Moreover, a hindered amine can be as a secondary alkanolamines that the amino group is attached to a secondary or a ternary carbon atom. Because of AMP forms bicarbonate through CO_2 absorption, thus, the acid gas loading is about one mole CO_2 per mole of amine so that for its regeneration lower energy is required [5]. AMP also reacts with CO_2 faster than MDEA that it is an advantage over MDEA. Aroua et al. [11] showed that the solubility of CO_2 in the aqueous MDEA+AMP with equal ratio is greater than the aqueous MDEA so that its loading value is between the aqueous AMP and aqueous MDEA.

In the recent years using the aqueous alkanolamines blended with some additive, which is known as chemical activator, is widely used to enhance the loading of the acid gases in solvent. Peparazine (Pz) is most commonly used as an chemical activator and in comparison to the other chemical activators is resistant to thermal and oxidative degradation and presents a higher rate of reaction. Additionally, the blended alkanolamines with Pz has low amine volatility because of non-ideality of the solvents [12].

Recently, the blended alkanolamines are widely studied to overcome the disadvantage of using a single alkanolamine. The mixed-alkanolamines consisting of a primary or secondary alkanolamine is blended with a tertiary alkanolamine that allows one to combine higher CO_2 loading of primary or secondary amines with higher selectivity of tertiary alkanolamines towards H_2S . Thus, using the mixed-solvent allows one to remove H_2S from the $\text{H}_2\text{S} + \text{CO}_2$ mixture so that CO_2 reaction with alkanolamine is taking place kinetically, because of the slow absorption of CO_2 [9]. Using a mixed-solvent of alkanolamines with appropriate molecular structure, an unstable carbamate ion may be formed in which it hydrolysis to bicarbonate ion so that the CO_2 gas loading of unity is achieved [4]. For selective removal of H_2S in the presence of CO_2 , a molecular structure for solvent may be designed that repress the formation of carbamate without influencing on the H_2S absorption [4].

At a gas sweetening process, absorption of sour gases is taking place in an absorption column at high acid gas partial pressure and low temperature so that the desorption for regeneration of the solvent occurs at high temperature and low acid gas partial pressure. So far a lot of data are given on the solubility of single acid gas in the one or mixed aqueous alkanolamines at the different pressure and temperature so that the available solubility data for CO_2 is more than H_2S . Moreover, the simultaneous data of the $\text{CO}_2 + \text{H}_2\text{S}$ solubility is needed for design an acid gas removal unit. Several works have been carried out for measurement of the solubility of the

mixture of CO₂ and H₂S in the aqueous alkanolamines. Ho and Eguren [13] measured the solubility of the H₂S + CO₂ in the aqueous MDEA and DEA solutions at 313 and 373 K. Jou et al. [14] measured the solubility H₂S+CO₂ in the aqueous MDEA solutions at 313 and 373 K. Savage et al. [15] obtained data on the simultaneous absorption of CO₂ + H₂S in the MDEA solution. They illustrated that MDEA is selective towards H₂S and the CO₂ absorption is controlled kinetically. Huttenhuis et al. [16] obtained the experimental data of the solubility of the H₂S + CO₂ simultaneously in MDEA with methane and nitrogen as the makeup gases so that it was concluded that type of the inert gas presents an influence on the H₂S solubility. However, the partial pressure of the CO₂ was not affected by type of the inert gas and the partial pressure of the H₂S enhances greatly with increasing the CO₂ loading. Lawson and Garst [17] measured the simultaneous absorption of CO₂+H₂S in MEA and DEA over wide range of acid gas composition and temperature. They compared their data with the others so that they made some assumptions in their calculations such as keeping water/amine ratio the same at the equilibrium condition. Mandal and Bandyopadhyay obtained the experimental data on the simultaneous solubility of H₂S + CO₂ in the aqueous solution of AMP+DEA [18] and MDEA+DEA [19]. They illustrated that the aqueous solution of AMP+DEA presents an efficient solvent for simultaneous absorption of CO₂ and H₂S [18]. Also, they suggested that for absorption of CO₂+H₂S simultaneously, it will be favorable to use the aqueous AMP with low composition of DEA. Moreover, they observed [19] that for the aqueous MDEA+AMP, the rate of absorption of CO₂ increases quickly with increasing DEA concentration in the blends, while that of H₂S increases to a much lesser extent. Thus, there is an expected decrease in the selectivity factor with increasing concentration of DEA. Blanchon Le Bouhelec-Tribouillois et al. [20] used a semi-synthetic apparatus to measure the solubility of the mixture of CO₂ and H₂S in the diethanolamine aqueous solution. They observed that at a fixed H₂S loading, injecting of CO₂ to the gas stream enhances the partial pressure of H₂S and CO₂ and vice versa. Lee et al. [21] and Jane et al. [8] obtained data on the solubility of mixture of CO₂ and H₂S in the aqueous DEA solution at 323 and 373 K and the aqueous DEA+AMP solution at 313 and 353 K, respectively. Yih and Sun [22] measured solubility of the CO₂+H₂S mixture in the aqueous DIPA solution. They studied the effect of the liquid and gas flow rates, temperature and liquid concentration on the absorption rate and selectivity factor. They concluded that the operation at low liquid and high gas flow rates, low temperature and low DIPA concentrations leads to selective removal of

H₂S from the acid gas mixtures. Li and Chang [23] measured the simultaneous absorption of CO₂+H₂S in the aqueous MEA+AMP mixture so that it was observed this amine mixture presents the higher H₂S and lower CO₂ loading capacities. Mandal et al. [24] investigated the selective absorption of H₂S from the N₂ streams containing H₂S and CO₂ into the aqueous solutions of AMP as well as MDEA. They found that the effect of gas-phase resistance on the absorption of H₂S was significant. Also they observed that the absorption of H₂S and the selectivity factor decreased at the same time for both solutions of alkanolamines so that with increasing amine concentration in the range 2.0-3.0 kmole/m³, the absorption of both CO₂ and H₂S were enhanced. Lu et al. [25] performed experimental investigation for selective absorption of H₂S from gas-mixed streams into the aqueous blend of MDEA and TBEE. They illustrated that the aqueous solution of MDEA+TBEE presents an efficient blend for selective H₂S removal. Godini and Mowla [26] performed investigation of selectivity for simultaneous absorption of H₂S and CO₂ from gaseous streams into an aqueous MEA solution. Their results revealed that performance of H₂S absorption in MEA is affected by pressure and amine concentration so that the selectivity of the amine solution is changed significantly. Qian et al. [27] investigated selective absorption of H₂S in MDEA from a gas mixture containing CO₂ that they observed H₂S removal efficiency rises with increasing in the liquid flow rate and declines with increasing in gas flow rate and temperature.

The several works have been carried out for measurement of the single acid gases such as CO₂ and H₂S in the blended alkanolamines [28, 29, 30]. However, the simultaneous solubility measurements of the CO₂+H₂S in the blended alkanolamines are rare and needs more investigations. In this work, the solubility data are obtained on the simultaneous absorption of CO₂+H₂S in the aqueous solutions of DIPA and MDEA, also in the aqueous solutions of mixed-alkanolamines such as MDEA+AMP, DIPA+AMP, MDEA+AMP+Pz and DIPA+AMP+Pz. The mass fraction of the total amine is fixed at 0.45 and the influence of blending AMP and Pz with aqueous MDEA and DIPA solutions are studied. Moreover, a comparison is carried out between the blends of MDEA-based and DIPA-based to find out the appropriate blend for maximum absorption of the acid gases. Finally, the solubility data are obtained under isothermal condition at 343 K and total pressure range of 0.1-2.1 MPa.

2. Experiment

2.1 Materials

The mixture of the CO₂+H₂S is supplied by Technical Gas Service Company with a fixed composition of 0.3 H₂S and 0.7 CO₂ in mole fraction with uncertainty of 0.005. The alkanolamines MDEA, DIPA and Pz were purchased with mass fraction purity > 0.99, 0.98 and 0.99, respectively, from Sigma-Aldrich. The AMP was supplied with mass fraction purity > 0.97 from Fluka. The specifications and sources of the supplied chemicals used in this work are summarized in Table 1. All of the materials were used without further purification. The aqueous mixed-alkanolamine systems were prepared using the deionized and degassed water. A digital balance with accuracy of ±0.001 g was used to weighting the water and alkanolamines.

2.2 Apparatus and procedure

The solubility data were obtained using a static high pressure apparatus which was described in details with its uncertainty of measuring instruments in the previous works [28, 29, 30]. The analysis of the gas phase was performed using a Gas Chromatograph (model Agilent 7890, a refinery gas analyzer). The deionized water was degassed by means of a water-filled ultrasonic bath. To prepare the specified aqueous solutions of alkanolamines, the water and alkanolamines were weighed using a digital balance. Following evacuating the equilibrium cell by employing a vacuum pump to discharge all of the remaining gas or liquid, the cell was fed by about 100 ml of the aqueous solution of alkanolamine and consequently, it was degassed. The temperature of the cell was set by means of a thermostated circulator and the pressure was monitored through a pressure transducer by recording the vapor pressure of the solution (P_v). The mixed-gas feed with constant composition (30% H₂S and 70% CO₂ in mole fraction) was introduced to the equilibrium cell through an injection cell. The number of moles of the injected CO₂ and H₂S gases are calculated as

$$n_{\text{CO}_2} = \frac{V_{\text{inj}}}{R} \left(\frac{0.7P_{\text{inj},1}}{T_{\text{inj},1}Z_1} - \frac{0.7P_{\text{inj},2}}{T_{\text{inj},2}Z_2} \right) \quad (1)$$

$$n_{\text{H}_2\text{S}} = \frac{V_{\text{inj}}}{R} \left(\frac{0.3P_{\text{inj},1}}{T_{\text{inj},1}Z_1} - \frac{0.3P_{\text{inj},2}}{T_{\text{inj},2}Z_2} \right) \quad (2)$$

where V_{inj} denotes the volume of the injection cell, R is universal gas constant, Z_1 and Z_2 are the compressibility factors of the H₂S+CO₂ mixture, respectively, corresponding to the initial

($P_{inj,1}$, $T_{inj,1}$) and final ($P_{inj,2}$, $T_{inj,2}$) conditions of the injection cell and the Peng–Robinson EoS was used to calculate their values. During absorption of the acid gases into the solvents, the stirrer was turning on until the equilibrium pressure is achieved (P_{tot}) so that no change in pressure is observed in 30 minutes interval. At this time, a gas sample was withdrawn from the gas phase and the compositions of the gas phase (y_{H_2S} and y_{CO_2}) was obtained using the GC. One should be noted that the equilibrium pressure of the CO_2+H_2S gas mixture ($P=P_{(CO_2+H_2S)}$) at each equilibrium state is calculated as

$$P = P_{tot} - P_v \quad (3)$$

and the equilibrium partial pressures of H_2S (P_{H_2S}) and CO_2 (P_{CO_2}) are calculated as

$$P_{CO_2} = y_{CO_2} P \quad (4)$$

$$P_{H_2S} = y_{H_2S} P \quad (5)$$

Moreover, the number moles of each acid gas in the gas phase at the equilibrium was computed as

$$n_{g,CO_2} = \frac{V_g P_{CO_2}}{ZRT} \quad (6)$$

$$n_{g,H_2S} = \frac{V_g P_{H_2S}}{ZRT} \quad (7)$$

where Z is the gas mixture compressibility factor and V_g denotes the volume of the gas phase that is the difference between the volume of the cell reactor and the volume of the liquid phase (V_l). The latter is obtained through measurement of the density of the amine solution using a 5.7 ml pycnometer at 343K. In this work, the several assumptions are made that it may cause uncertainty. For example, the water/amine ratio in the liquid phase is assumed to be the same as the initial water/amine ratio introducing to the reactor cell. Another uncertainty is the volume expansion in the liquid phase that was caused by dissolving of the acid gases so that it is assumed V_l not changing before and after the experiments. Finally, acid gas loading which is defined as the moles of the acid gas per total moles of amine (α_{CO_2} , α_{H_2S}) and the mole fraction of dissolved acid gases (x_{CO_2} , x_{H_2S}) are calculated as

$$\alpha_{CO_2} = \frac{n_{CO_2} - n_{g,CO_2}}{n_{amine}} \quad (8)$$

$$\alpha_{H_2S} = \frac{n_{H_2S} - n_{g,H_2S}}{n_{amine}} \quad (9)$$

$$x_{CO_2} = \frac{\alpha_{CO_2} \cdot n_{amine}}{\alpha_{CO_2} \cdot n_{amine} + n_{amine} + n_{water}} \quad (10)$$

$$x_{H_2S} = \frac{\alpha_{H_2S} \cdot n_{amine}}{\alpha_{H_2S} \cdot n_{amine} + n_{amine} + n_{water}} \quad (11)$$

3. Results and discussion

In the previous work [30], the validation of the density data was carried out using pycnometer through measuring the density of pure water at 300–360 K and comparing with the literature [31]. The density of the aqueous alkanolamine systems was measured at 343K at the given concentration as presented in Table 2. The combined expanded uncertainty U_c of the measurements with level of confidence of 0.95 was founded 0.5 kg.m^{-3} .

It is difficult to validate the present experimental apparatus and procedure for the absorption of the CO_2+H_2S mixture simultaneously into the solvents with the given data in the literature, because of lack of having utterly the same acid gases composition in the open literature. Hence, the solubility of the single acid gases in the aqueous solutions of alkanolamines was measured and compared with those given in the literature. These comparisons were presented in the previous works for the solubility of CO_2 [28, 29] and for the solubility of H_2S [30] in the aqueous solution of alkanolamines.

In this work, the simultaneous absorption of the CO_2+H_2S mixture was measured in the prepared aqueous alkanolamine solutions at 343 K and total pressure range of 0.1-2.1 MPa. A feed gas with the constant gas compositions was used and the compositions of the aqueous DIPA-based solutions are as DIPA (45) mass %, DIPA+AMP (25+20) mass %, DIPA+AMP+Pz (25+15+5) mass %, DIPA+AMP+Pz (25+10+10) mass % and DIPA+AMP+Pz (25+5+15) mass %. The mass compositions of the aqueous MDEA-based solutions are as MDEA (45) mass %, MDEA+AMP (25+20) mass %, MDEA+AMP+Pz (25+15+5) mass %, MDEA+AMP+Pz (25+10+10) mass % and MDEA+AMP+Pz (25+5+15) mass % so that the total amine mass fraction for the both DIPA and MDEA mixtures was fixed at 0.45. The compiled solubility data

are presented in Tables 3 and 4 as the H₂S and CO₂ partial pressure against their loading, mole fraction and uncertainties. Also, the partial pressure of CO₂ versus its loading is plotted for the aqueous solutions of the MDEA-based and DIPA-based, respectively, as shown in Figs. 1 and 2. Figs. 3 and 4 present the partial pressure of the H₂S versus its loading for the aqueous solutions of the MDEA-based and DIPA-based, respectively. The error propagation theory by Shoemaker [32] was used to calculate the uncertainties of the calculated variables [33]. Following this theory, if s, \dots, u are the measured quantities with uncertainties $\delta s, \dots, \delta u$, then the uncertainty δq of the calculated variable $q(s, \dots, u)$ is given as

$$\delta q = \pm \sqrt{\left(\frac{\partial q}{\partial s} \delta s\right)^2 + \dots + \left(\frac{\partial q}{\partial u} \delta u\right)^2} \quad (12)$$

One should be noted that the uncertainty of the solubility of H₂S+CO₂ in the aqueous alkanolamine systems was estimated through the uncertainties of all the legal documents which were utilized in this study.

As the Fig. 1 illustrates, at the acid gas loading less than about 0.55 the CO₂ loading increases through substituting 20 mass% MDEA with AMP. It should be emphasized AMP is a sterically hindered amine that forms unstable carbamate in reaction with CO₂ in which it is dissipated by little heat and its reaction with CO₂ is intensified more than MDEA so that it provides a CO₂ absorption loading about one mol CO₂ per mole amine [5]. Although the CO₂ absorption strength of AMP is higher than MDEA, but its rate is controlled kinetically so that following loading about 0.55, the aqueous MDEA solution acts as a better absorbent than the aqueous MDEA+AMP solution so that its loading is higher. Blending some Pz with the aqueous solution of MDEA+AMP leads to intensify its reaction rate with CO₂. Thus, as shown in Fig. 1, the loading is improved by substituting 5, 10 and 15 mass% AMP with Pz so that as the ratio of Pz/AMP increases, loading is improved too. Yang et al.'s work [34] showed the same behavior for the solubility of CO₂ in the aqueous solutions of AMP+PZ that by increasing the ratio of the Pz/AMP the CO₂ loading enhances.

As Fig. 2 demonstrates, the aqueous solution of 45 mass% DIPA presents the lowest CO₂ loading, however through substituting 20 mass% DIPA with AMP the loading increases. Thus, one can see DIPA presents its selectivity towards H₂S over CO₂ so that the absorption strength of DIPA toward CO₂ reduces. As a result, using AMP can improve the absorption of CO₂ in the aqueous solution of DIPA+AMP [4]. By increasing Pz mass% and reducing AMP%, similar to

the aqueous solution of MDEA-based, it is observed that the loading is improved in the aqueous solution of DIPA-based. Because Pz similar to AMP intensifies the reaction rate with CO_2 and leads to overcome the selective removal of H_2S by DIPA. Dash et al. [12] illustrated that the mixed AMP-Pz presents higher loading of CO_2 due to Pz and high absorption capacity towards CO_2 due to AMP. In general, in the presence of the H_2S , AMP and Pz improve the absorption of CO_2 into aqueous solutions of MDEA and DIPA.

As the Fig. 3 displays, the aqueous 45 mass% MDEA system presents the highest H_2S loading that it refers to selective removal of the MDEA towards H_2S in the presence of the CO_2 so that this aqueous solution has presented the lowest CO_2 loading. The H_2S loading reduces through substituting 20 mass% MDEA with AMP. As a result, using the mixed AMP-MDEA at constant mass fraction leads to lower the H_2S loading and intensifies the CO_2 loading. Moreover, even substituting 5, 10 and 15 mass% AMP with Pz, it is observed that the H_2S loading decreases further so that Pz as a chemical activator similar to AMP enhances the strength of CO_2 absorption.

Fig. 4 demonstrates the partial pressure of the H_2S versus its loading in the aqueous DIPA-based solutions. As one can see, unlike the MDEA-based solution, by substituting 20 mass% MDEA with AMP, the H_2S absorption of this solution enhances. It is demonstrated [35, 36] that AMP may presents a great selectivity towards H_2S over CO_2 so that AMP improves the selectivity of the DIPA solution and increases the absorption of H_2S so that this shows that selectivity of AMP is greater than DIPA. On the other hand, AMP intensifies the reaction with CO_2 so that the absorption of the CO_2 is improved as shown in Fig. 2. On the other hand as shown in Fig. 3, it is observed that substituting AMP with 20 mass % MDEA, the absorption of the H_2S decreases as discussed before that is due to selectivity of the solution towards H_2S . It should be noted that MDEA, DIPA and AMP are known as a selective alkanolamine towards H_2S but the question is which one results a higher degree of selectivity. By comparison the results, it can be concluded that order of the H_2S selectivity is as $\text{MDEA} > \text{AMP} > \text{DIPA}$ as shown in Figs. 5 (b), 3 and 4. As shown in Fig. 4, thus, increasing Pz and decreasing AMP in the DIPA-based systems leads to reduction of the H_2S loading. Generally in the presence of the CO_2 , Pz reduces the absorption of the H_2S in the aqueous MDEA-based and DIPA-based systems. Also in the presence of the CO_2 the absorption of the H_2S decreases and increases in the aqueous AMP-MDEA and AMP-DIPA systems, respectively.

Figs. 5 to 9 show a comparison between the aqueous MDEA-based and DIPA-based systems through the partial pressure of the CO₂ and H₂S versus their loading. As Figs 5-9 (b) show, the absorption of the H₂S in presence of the CO₂ using the aqueous MDEA-based systems presents better performance respect to the aqueous DIPA-based systems so that it is demonstrated selectivity of the MDEA towards H₂S is better than DIPA. As shown in Fig. 5 (a), prior the loading about 0.5, the aqueous DIPA system presents higher CO₂ loading than the aqueous MDEA system so that following the loading 0.5 this behavior is reversed. Since DIPA and MDEA are the secondary and tertiary alkanolamines, respectively, thus, DIPA shows higher CO₂ absorption capacity. Therefore, at the beginning of the absorption, the DIPA system absorbs CO₂ better, however, following the loading of about 0.5; the solution becomes saturated while the aqueous MDEA solution presents still its capacity to absorb more CO₂. By substituting 20 mass% DIPA and MDEA with AMP, as Fig. 6 (a) shows, AMP intensifies the CO₂ absorption capacity of MDEA so that it compensates disadvantage of the MDEA in low rate of CO₂ absorption. Moreover, following substituting 5, 10 and 15 mass% AMP with Pz, it is observed that the CO₂ loading of the aqueous MDEA-based and DIPA-based systems are close to each other as shown in Figs. 7-9 (a), because the CO₂ absorption capacity of both the aqueous MDEA-based and DIPA-based systems enhances through using Pz.

Figs. 10 and 11 show a comparison of the solubility of the acid gases in all of the aqueous DIPA-based and MDEA-based systems. As these figures demonstrate, the aqueous DIPA+AMP+Pz (25+5+15) mass% system presents highest CO₂ loading that it is a good blended solvent for absorption of the CO₂ in the presence of the H₂S and on the other hand, the aqueous MDEA 45 mass% presents a very good solvent for higher H₂S loading over CO₂.

4. Conclusions

In this work, the solubility of the CO₂+H₂S mixture were measured in blends of the aqueous alkanolamines at 343 K and pressure range 0.1-2.1 MPa. The mass fraction of the total amine was fixed at 0.45. Composition of the aqueous DIPA-based systems were as DIPA (45) mass %, DIPA+AMP (25+20) mass %, DIPA+AMP+Pz (25+15+5) mass %, DIPA+AMP+Pz (25+10+10) mass % and DIPA+AMP+Pz (25+5+15) mass %. The composition of the aqueous MDEA-based systems were as MDEA (45) mass %, MDEA+AMP (25+20) mass %, MDEA+AMP+Pz (25+15+5) mass %, MDEA+AMP+Pz (25+10+10) mass % and MDEA+AMP+Pz (25+5+15) mass %.

MDEA+AMP+Pz (25+15+5) mass %, MDEA+AMP+Pz (25+10+10) mass % and MDEA+AMP+Pz (25+5+15) mass %.

In both of the aqueous DIPA-based and MDEA-based systems, AMP and Pz enhance the loading of the CO₂ in the presence of the H₂S. Also in the presence of the CO₂, Pz decreases absorption of the H₂S into both the aqueous MDEA-based and DIPA-based systems. Moreover in the presence of the CO₂, AMP reduces and enhances the absorption of the H₂S into the aqueous MDEA-based systems and the aqueous DIPA-based systems, respectively. It was concluded that the degree of selectivity of the alkanolamine toward H₂S is as MDEA>AMP>DIPA. Finally, the aqueous DIPA+AMP+Pz (25+5+15) mass % system presented an efficient solvent to removing CO₂ in presence of H₂S and the aqueous 45 mass % MDEA system is a good absorber for absorption of the H₂S in the presence of CO₂.

Nomenclature

<i>n</i>	number of mole
<i>P</i>	pressure
<i>R</i>	gas constant
<i>T</i>	temperature in Kelvin
<i>u</i>	uncertainty
<i>V</i>	volume
<i>x</i>	liquid phase mole fraction
<i>y</i>	vapor phase mole fraction
<i>Z</i>	compressibility factor

Subscripts

<i>CO₂</i>	carbon dioxide
<i>H₂S</i>	hydrogen sulfide
<i>inj</i>	injection cell
<i>g</i>	gas phase
<i>l</i>	liquid phase
<i>tot</i>	total
<i>v</i>	vapor
1	before injection
2	after injection

Greek letters

α	CO ₂ or H ₂ S loading in liquid phase, mole of gas/mole of amine
ρ	density

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Table 1: The specifications and sources of chemicals used in this work.

Chemical Name	Molecular formula	Supplier	Purity(mass fraction)
N-methyldiethanolamine (MDEA)	$CH_3N(CH_2CH_2OH)_2$	Aldrich	>0.99
Diisopropanolamine (DIPA)	$C_6H_{15}NO_2$	Aldrich	>0.98
Piperazine (Pz)	$C_4H_{10}N_2$	Aldrich	>0.99
2-amino-2-methyl-1-propanol (AMP)	$(CH_3)_2C(NH_2)CH_2OH$	Fluka	>0.97
Mixture of the CO_2+H_2S	$CO_2 + H_2S$	Technical Gas Service Company	0.7 $CO_2+0.3 H_2S$ in mole fraction ^a

^a Standard uncertainty u is $u(\text{mole fraction}) = 0.005$.

Table 2: Values of density ρ at temperature of 343K for the aqueous solutions of alkanolamines that are used in this work.^a

Type of aqueous solution	$\rho / kg . m^{-3}$	Refs
MDEA (45) mass %	1003.5	This work
MDEA + AMP (25+20) mass %	989.6	[30]
MDEA + AMP + Pz (25+15+5) mass %	994.0	[30]
MDEA + AMP + Pz (25+10+10) mass %	1001.5	[30]
MDEA + AMP + Pz (25+5+15) mass %	1002.8	[30]
DIPA (45) mass %	996.8	This work
DIPA + AMP (25+20) mass %	981.5	This work
DIPA + AMP + Pz (25+15+5) mass %	986.5	This work
DIPA + AMP + Pz (25+10+10) mass %	991.1	This work
DIPA + AMP + Pz (25+5+15) mass %	996.4	This work

^a Combined expanded uncertainty : $U_c(\rho) = 0.5 kg \cdot m^{-3}$ (0.95 level of confidence).

Table 3: The experimental (vapor+liquid) equilibrium data for loading α , liquid and gas phase mole fraction x and y , pressure p with standard uncertainty $u(x)$ for simultaneous solubility of $CO_2 + H_2S$ in the aqueous systems of DIPA, DIPA+AMP and DIPA+AMP+Pz at 343 K.^a

α_{CO_2}	x_{CO_2}	y_{CO_2}	P_{CO_2} / MPa	$u(x_{CO_2})$	α_{H_2S}	x_{H_2S}	y_{H_2S}	P_{H_2S} / MPa	$u(x_{H_2S})$	P_{tot} / MPa
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DIPA (45) mass %

0.3714	0.0351	0.7172	0.173	0.0002	0.1604	0.0154	0.2828	0.068	0.0002	0.266
0.4375	0.0410	0.7057	0.429	0.0004	0.1886	0.0181	0.2943	0.179	0.0001	0.632
0.4666	0.0436	0.7187	0.647	0.0001	0.2052	0.0197	0.2813	0.253	0.0001	0.924
0.4818	0.0450	0.7175	0.779	0.0002	0.2126	0.0204	0.2825	0.307	0.0001	1.111
0.4953	0.0462	0.7195	0.923	0.0001	0.2205	0.0211	0.2805	0.360	0.0002	1.307
0.5108	0.0476	0.7111	1.061	0.0003	0.2247	0.0215	0.2889	0.431	0.0002	1.516
0.5186	0.0483	0.7166	1.187	0.0001	0.2317	0.0221	0.2834	0.470	0.0003	1.681
0.5259	0.0489	0.7152	1.270	0.0001	0.2351	0.0225	0.2848	0.506	0.0001	1.800
0.5323	0.0495	0.7151	1.355	0.0002	0.2385	0.0228	0.2849	0.540	0.0002	1.919

DIPA+AMP (25+20) mass %

0.3379	0.0379	0.7537	0.038	0.0001	0.1459	0.0167	0.2463	0.047	0.0002	0.110
0.4519	0.0501	0.7464	0.341	0.0001	0.1989	0.0227	0.2536	0.116	0.0001	0.480
0.4904	0.0541	0.7261	0.567	0.0002	0.2154	0.0245	0.2739	0.214	0.0001	0.806
0.5067	0.0558	0.7234	0.715	0.0002	0.2233	0.0254	0.2765	0.273	0.0002	1.013
0.5169	0.0569	0.7248	0.823	0.0001	0.2291	0.0260	0.2751	0.312	0.0002	1.159
0.5255	0.0578	0.7320	0.964	0.0001	0.2366	0.0268	0.2680	0.353	0.0003	1.341
0.5357	0.0588	0.7339	1.120	0.0003	0.2439	0.0277	0.2661	0.406	0.0002	1.550
0.5447	0.0597	0.7306	1.247	0.0002	0.2485	0.0282	0.2693	0.460	0.0001	1.730

DIPA+AMP+Pz (25+15+5) mass %

0.4154	0.0464	0.7496	0.128	0.0002	0.1801	0.0207	0.2504	0.043	0.0004	0.194
0.5118	0.0566	0.6822	0.498	0.0002	0.2161	0.0247	0.3178	0.232	0.0001	0.754
0.5375	0.0592	0.6905	0.742	0.0002	0.2278	0.0260	0.3094	0.333	0.0001	1.098
0.5445	0.0600	0.6964	0.831	0.0001	0.2322	0.0265	0.3035	0.362	0.0002	1.217
0.5526	0.0608	0.7012	0.926	0.0001	0.2371	0.0270	0.2988	0.395	0.0002	1.344
0.5585	0.0614	0.7031	1.028	0.0002	0.2404	0.0274	0.2969	0.434	0.0003	1.485
0.5628	0.0618	0.7054	1.110	0.0003	0.2434	0.0277	0.2945	0.463	0.0003	1.597
0.5689	0.0625	0.7060	1.214	0.0001	0.2465	0.0281	0.2939	0.505	0.0002	1.742
0.5733	0.0629	0.7033	1.275	0.0004	0.2473	0.0281	0.2967	0.538	0.0001	1.836

DIPA+AMP+Pz (25+10+10) mass %

0.4397	0.0492	0.5983	0.095	0.0001	0.1845	0.0213	0.4017	0.064	0.0001	0.182
0.5422	0.0600	0.6405	0.458	0.0001	0.2217	0.0254	0.3595	0.257	0.0002	0.739
0.5619	0.0621	0.6469	0.614	0.0002	0.2278	0.0261	0.3531	0.335	0.0002	0.972
0.5689	0.0628	0.6583	0.712	0.0003	0.2318	0.0266	0.3417	0.370	0.0002	1.105
0.5780	0.0638	0.6578	0.794	0.0002	0.2338	0.0268	0.3422	0.413	0.0001	1.231
0.5896	0.0650	0.6653	0.932	0.0001	0.2390	0.0274	0.3346	0.469	0.0003	1.424
0.6001	0.0660	0.6604	1.035	0.0002	0.2396	0.0274	0.3396	0.532	0.0001	1.591
0.6116	0.0672	0.6572	1.170	0.0008	0.2402	0.0275	0.3427	0.610	0.0002	1.803
0.6133	0.0674	0.6644	1.235	0.0006	0.2429	0.0278	0.3356	0.624	0.0002	1.882

DIPA+AMP+Pz (25+5+15) mass %

0.4575	0.0512	0.5503	0.076	0.0002	0.1910	0.0220	0.4496	0.062	0.0001	0.161
0.5652	0.0625	0.5766	0.391	0.0001	0.2212	0.0254	0.4234	0.287	0.0003	0.700
0.5831	0.0644	0.6017	0.543	0.0003	0.2269	0.0261	0.3983	0.360	0.0001	0.925
0.5932	0.0654	0.6161	0.652	0.0001	0.2305	0.0265	0.3838	0.406	0.0003	1.081
0.5978	0.0659	0.6321	0.744	0.0001	0.2342	0.0269	0.3678	0.433	0.0003	1.200
0.6107	0.0672	0.6388	0.883	0.0002	0.2378	0.0273	0.3612	0.499	0.0001	1.405
0.6210	0.0683	0.6430	1.018	0.0002	0.2400	0.0275	0.3570	0.565	0.0002	1.606
0.6281	0.0690	0.6535	1.175	0.0001	0.2440	0.0280	0.3465	0.623	0.0002	1.821

^a Standard uncertainties: $u(T)=0.01K$, $u(P_{acid\ gas})=0.0007$ MPa and $u(\text{amine mass fraction})=0.001$

Table 4: The experimental (vapor+liquid) equilibrium data for loading α , liquid and gas phase mole fraction x and y , pressure p with standard uncertainty $u(x)$ for simultaneous solubility of $\text{CO}_2 + \text{H}_2\text{S}$ in the aqueous systems of MDEA, MDEA+AMP and MDEA+AMP+Pz at 343 K.^a

α_{CO_2}	x_{CO_2}	y_{CO_2}	$P_{\text{CO}_2} / \text{MPa}$	$u(x_{\text{CO}_2})$	$\alpha_{\text{H}_2\text{S}}$	$x_{\text{H}_2\text{S}}$	$y_{\text{H}_2\text{S}}$	$P_{\text{H}_2\text{S}} / \text{MPa}$	$u(x_{\text{H}_2\text{S}})$	$P_{\text{tot}} / \text{MPa}$
MDEA (45) mass %										
0.2447	0.0244	0.8729	0.159	0.0002	0.1142	0.0115	0.1271	0.023	0.0001	0.205
0.3366	0.0332	0.8545	0.299	0.0002	0.1604	0.0161	0.1455	0.051	0.0001	0.372
0.3903	0.0383	0.8346	0.420	0.0001	0.1878	0.0188	0.1654	0.083	0.0002	0.526
0.4558	0.0445	0.8166	0.657	0.0001	0.2244	0.0224	0.1834	0.148	0.0003	0.827
0.4883	0.0475	0.8210	0.906	0.0002	0.2513	0.0250	0.1790	0.198	0.0002	1.127
0.5576	0.0539	0.8063	1.035	0.0003	0.2831	0.0281	0.1936	0.249	0.0002	1.307
0.5737	0.0554	0.8049	1.235	0.0003	0.2989	0.0296	0.1951	0.299	0.0001	1.557
0.5908	0.0569	0.8008	1.485	0.0001	0.3161	0.0313	0.1992	0.369	0.0004	1.877
MDEA+ AMP (25+20) mass %										
0.3869	0.0452	0.8245	0.196	0.0002	0.1735	0.0208	0.1755	0.042	0.0001	0.261
0.4713	0.0545	0.7962	0.414	0.0002	0.2152	0.0256	0.2038	0.106	0.0001	0.542
0.5196	0.0597	0.7906	0.694	0.0004	0.2442	0.0290	0.2094	0.184	0.0002	0.901
0.5362	0.0615	0.7850	0.847	0.0001	0.2551	0.0302	0.2150	0.232	0.0002	1.102
0.5458	0.0626	0.7829	0.965	0.0001	0.2627	0.0311	0.2171	0.267	0.0001	1.255
0.5540	0.0634	0.7827	1.084	0.0002	0.2704	0.0320	0.2173	0.301	0.0003	1.408
0.5613	0.0642	0.7849	1.245	0.0003	0.2799	0.0331	0.2151	0.341	0.0003	1.609
0.5679	0.0649	0.7802	1.352	0.0002	0.2850	0.0337	0.2198	0.381	0.0001	1.756
0.5752	0.0657	0.7779	1.528	0.0002	0.2932	0.0346	0.2221	0.436	0.0004	1.987
MDEA+AMP+Pz (25+15+5) mass %										
0.3840	0.0449	0.7495	0.130	0.0002	0.1666	0.0200	0.2505	0.043	0.0001	0.197
0.4780	0.0553	0.7468	0.341	0.0002	0.2100	0.0251	0.2532	0.116	0.0001	0.481
0.5158	0.0595	0.7449	0.514	0.0001	0.2286	0.0272	0.2551	0.176	0.0002	0.713
0.5347	0.0615	0.7505	0.642	0.0003	0.2397	0.0285	0.2495	0.213	0.0003	0.879
0.5510	0.0633	0.7508	0.789	0.0001	0.2495	0.0297	0.2492	0.262	0.0003	1.074
0.5658	0.0648	0.7502	0.961	0.0001	0.2590	0.0308	0.2498	0.320	0.0002	1.305
0.5774	0.0661	0.7487	1.126	0.0004	0.2667	0.0316	0.2513	0.378	0.0002	1.527
0.5859	0.0670	0.7521	1.285	0.0002	0.2748	0.0326	0.2479	0.424	0.0001	1.732
0.5902	0.0675	0.7489	1.344	0.0002	0.2771	0.0328	0.2510	0.450	0.0001	1.818
MDEA+AMP+Pz (25+10+10) mass %										
0.4093	0.0481	0.6644	0.097	0.0003	0.1742	0.0211	0.3356	0.049	0.0001	0.169
0.5201	0.0604	0.6985	0.363	0.0002	0.2227	0.0268	0.3015	0.157	0.0002	0.542
0.5499	0.0636	0.7081	0.535	0.0002	0.2371	0.0284	0.2919	0.221	0.0002	0.778
0.5631	0.0650	0.7069	0.634	0.0001	0.2428	0.0291	0.2931	0.263	0.0002	0.920
0.5756	0.0664	0.7080	0.747	0.0001	0.2488	0.0298	0.2919	0.308	0.0003	1.077
0.5909	0.0680	0.7143	0.925	0.0002	0.2578	0.0309	0.2857	0.370	0.0001	1.318
0.6035	0.0694	0.7118	1.088	0.0003	0.2633	0.0315	0.2882	0.440	0.0003	1.551
0.6112	0.0702	0.7186	1.238	0.0001	0.2702	0.0323	0.2814	0.485	0.0001	1.745

0.6136 0.0704 0.7166 1.272 0.0002 | 0.2709 0.0324 0.2834 0.503 0.0002 | 1.797

MDEA+AMP+Pz (25+5+15) mass %

0.4309	0.0505	0.6339	0.093	0.0002	0.1825	0.0220	0.3660	0.054	0.0001	0.169
0.5527	0.0639	0.6490	0.401	0.0003	0.2294	0.0276	0.3509	0.216	0.0001	0.638
0.5759	0.0664	0.6586	0.549	0.0001	0.2384	0.0286	0.3414	0.284	0.0002	0.856
0.5899	0.0679	0.6603	0.661	0.0001	0.2429	0.0291	0.3397	0.340	0.0002	1.023
0.5995	0.0690	0.6673	0.7601	0.0003	0.2473	0.0296	0.3327	0.379	0.0003	1.161
0.6081	0.0699	0.6723	0.869	0.0002	0.2511	0.0301	0.3277	0.423	0.0002	1.314
0.6164	0.0708	0.6797	1.005	0.0001	0.2558	0.0306	0.3203	0.473	0.0002	1.500
0.6234	0.0715	0.6900	1.167	0.0004	0.2618	0.0313	0.3099	0.524	0.0003	1.714

^a Standard uncertainties: $u(T)=0.01\text{K}$, $u(P_{\text{acid gas}})=0.0007\text{ MPa}$ and $u(\text{amine mass fraction})=0.001$

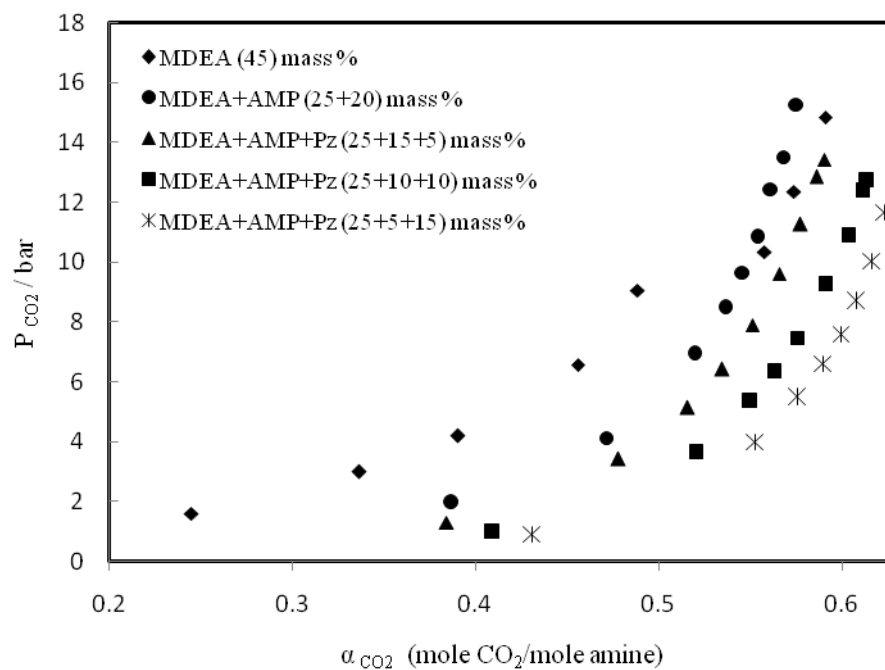


Fig. 1. Partial pressure of the CO₂ versus its loading for solubility of the CO₂ in presence of the H₂S in aqueous solutions of MDEA, MDEA+AMP, MDEA+AMP+Pz at 343 K.

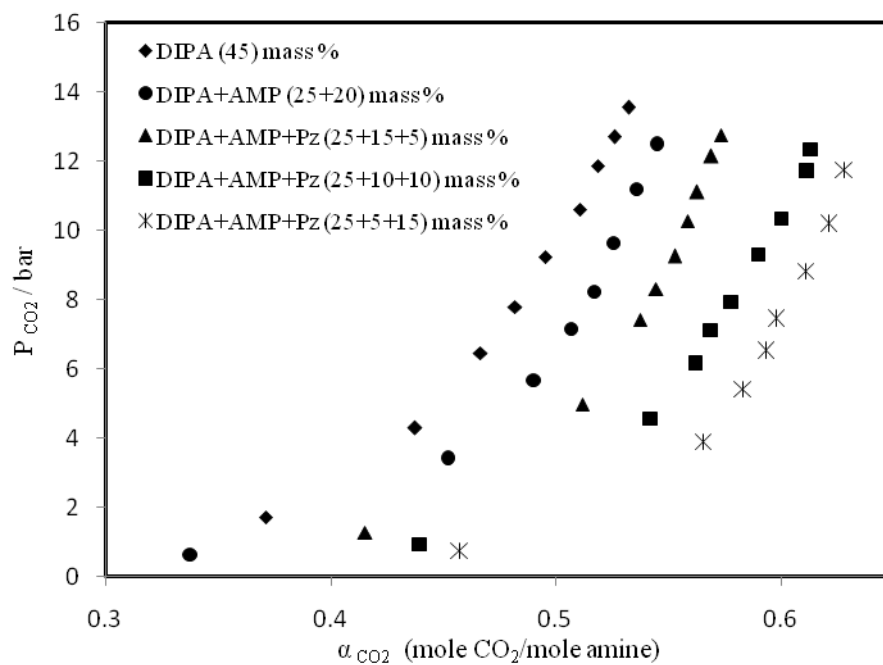


Fig. 2. Partial pressure of the CO₂ versus its loading for solubility of the CO₂ in presence of the H₂S in aqueous solutions of DIPA, DIPA+AMP, DIPA+AMP+Pz at 343 K.

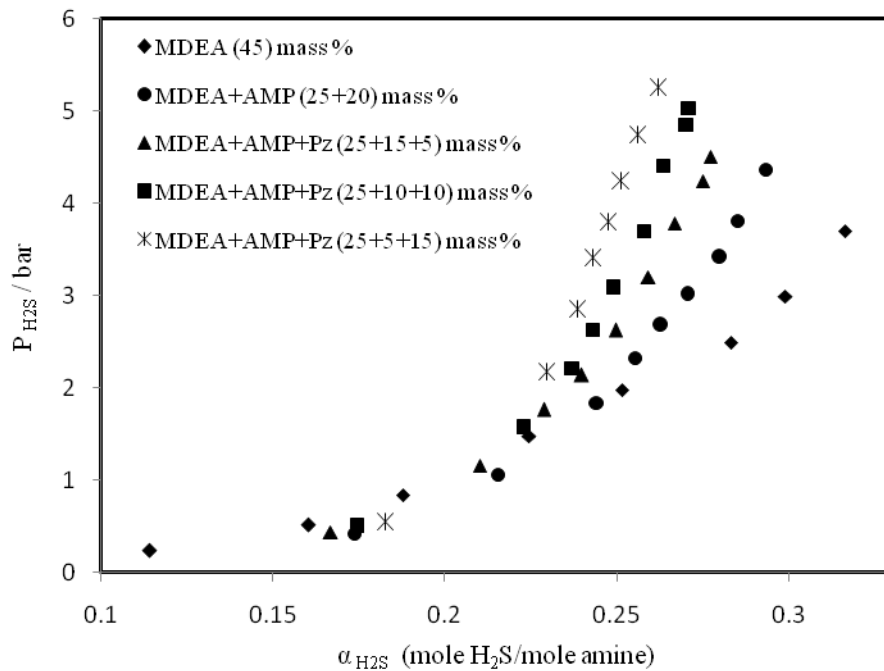


Fig. 3. Partial pressure of the H_2S versus its loading for solubility of the H_2S in presence of the CO_2 in aqueous solutions of MDEA, MDEA+AMP, MDEA+AMP+Pz at 343 K.

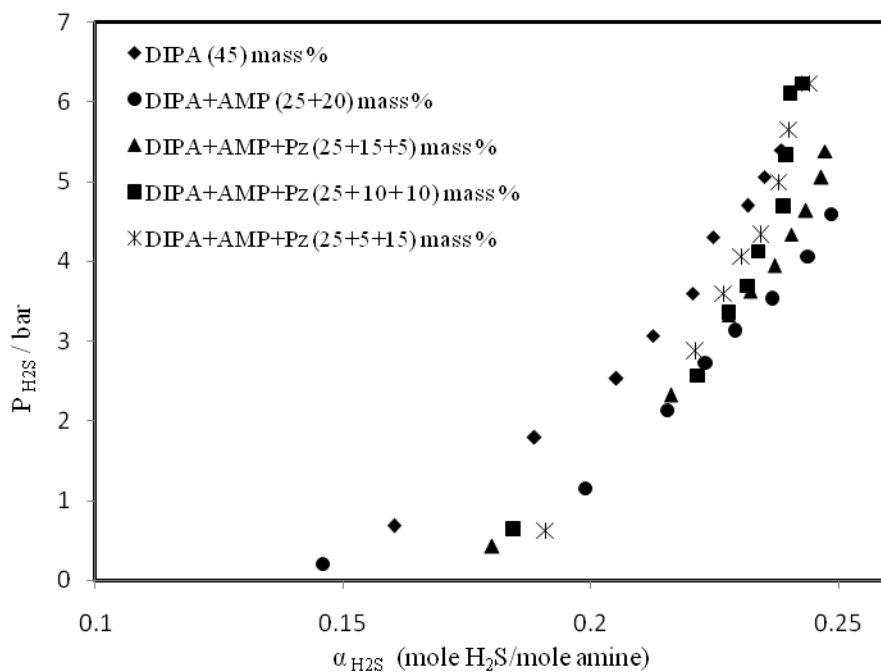


Fig. 4. Partial pressure of the H_2S versus its loading for solubility of the H_2S in presence of the CO_2 in aqueous solutions of DIPA, DIPA+AMP, DIPA+AMP+Pz at 343 K.

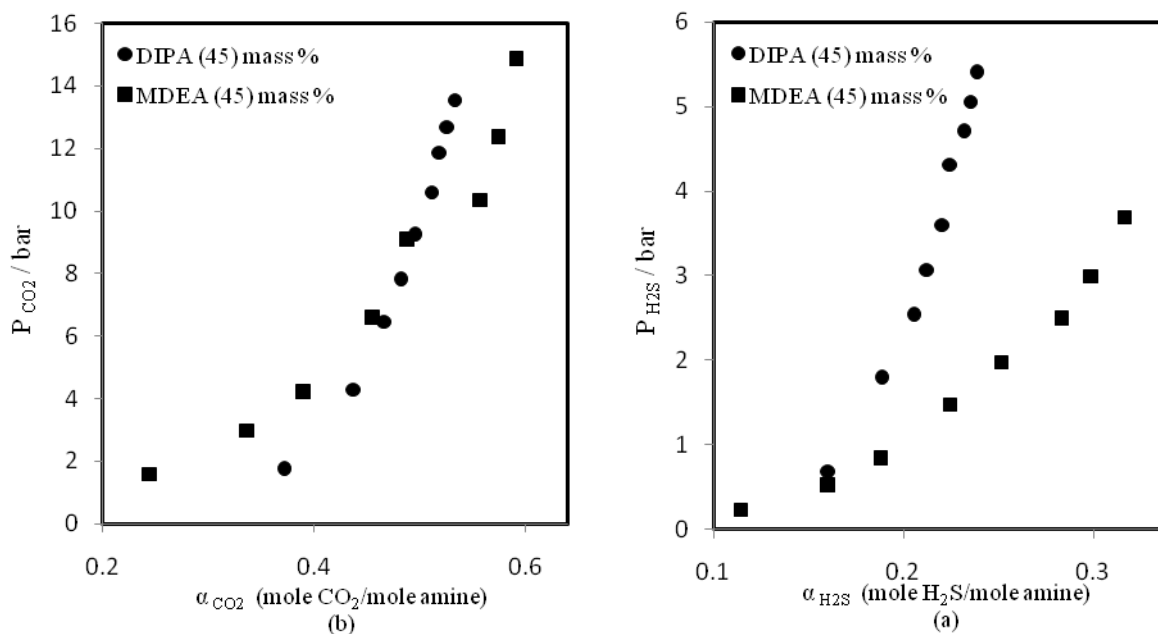


Fig. 5. Comparison between aqueous solutions of the 45 mass % MDEA and 45 mass % DIPA to absorb. (a) H₂S in the presence of the CO₂. (b) CO₂ in the presence of the H₂S.

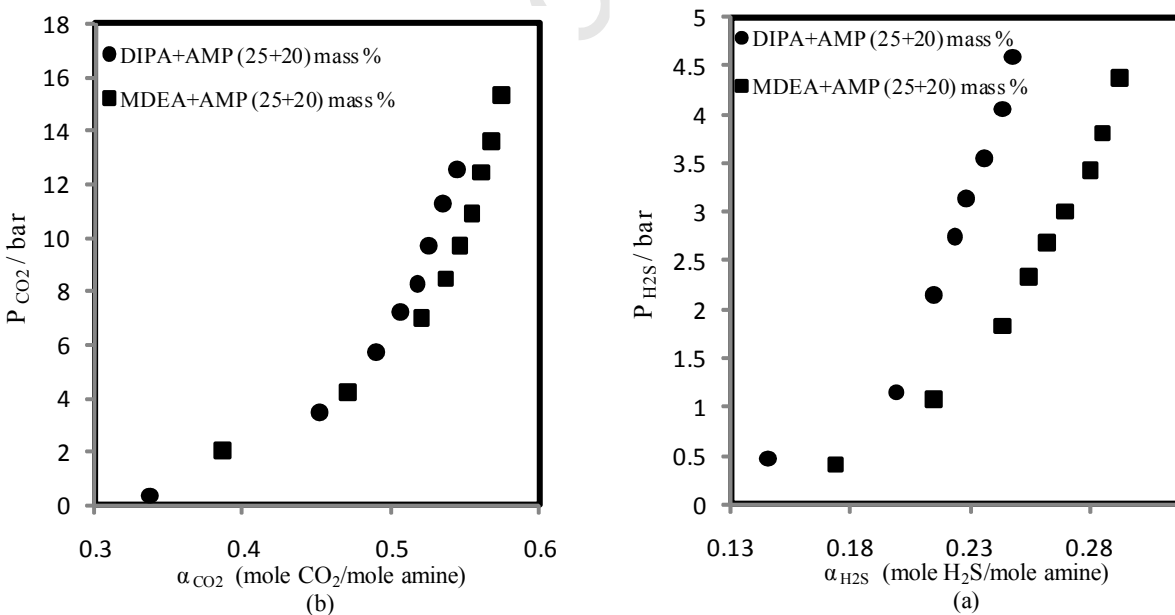


Fig. 6. Comparison between aqueous solutions of MDEA+AMP (25+20) mass % and DIPA+AMP (25+20) mass % to absorb. (a) H₂S in the presence of the CO₂. (b) CO₂ in the presence of the H₂S.

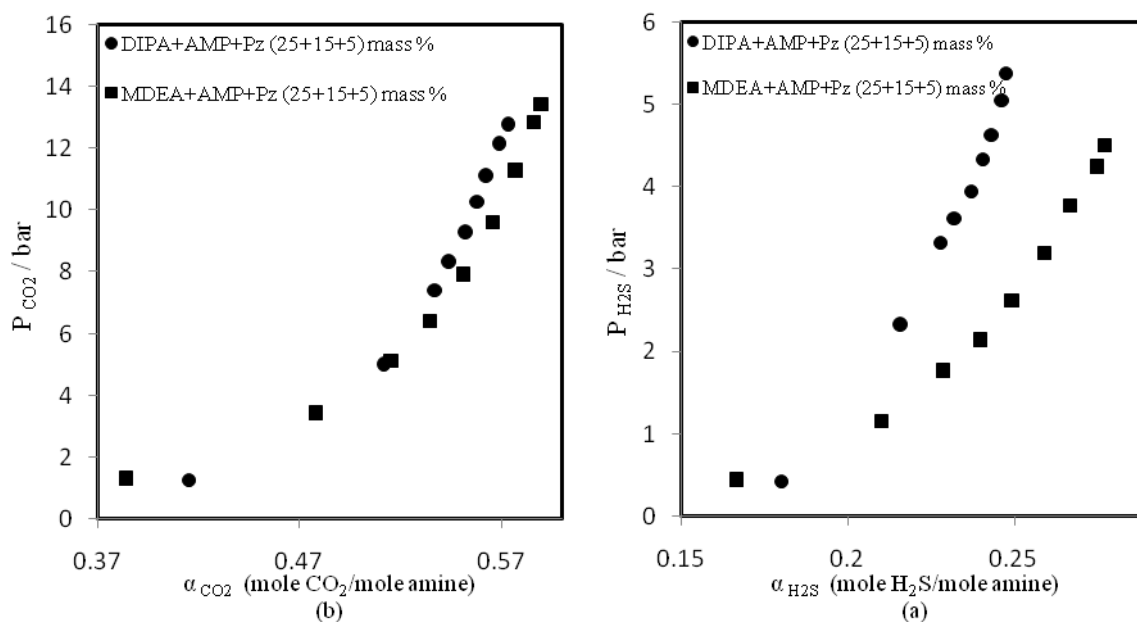


Fig. 7. Comparison between aqueous solutions of MDEA+AMP+Pz (25+15+5) mass % and DIPA+AMP+Pz (25+15+5) mass % to absorb. (a) H₂S in the presence of the CO₂. (b) CO₂ in the presence of the H₂S.

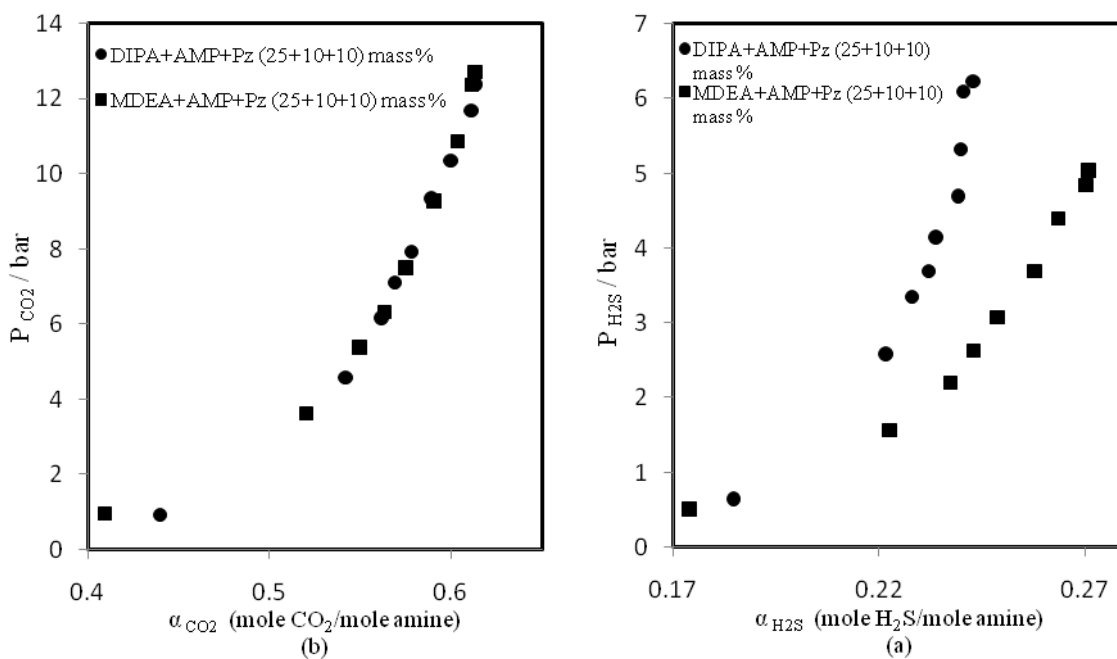


Fig. 8. Comparison between aqueous solutions of MDEA+AMP+Pz (25+10+10) mass % and DIPA+AMP+Pz (25+10+10) mass % to absorb. (a) H₂S in the presence of the CO₂. (b) CO₂ in the presence of the H₂S.

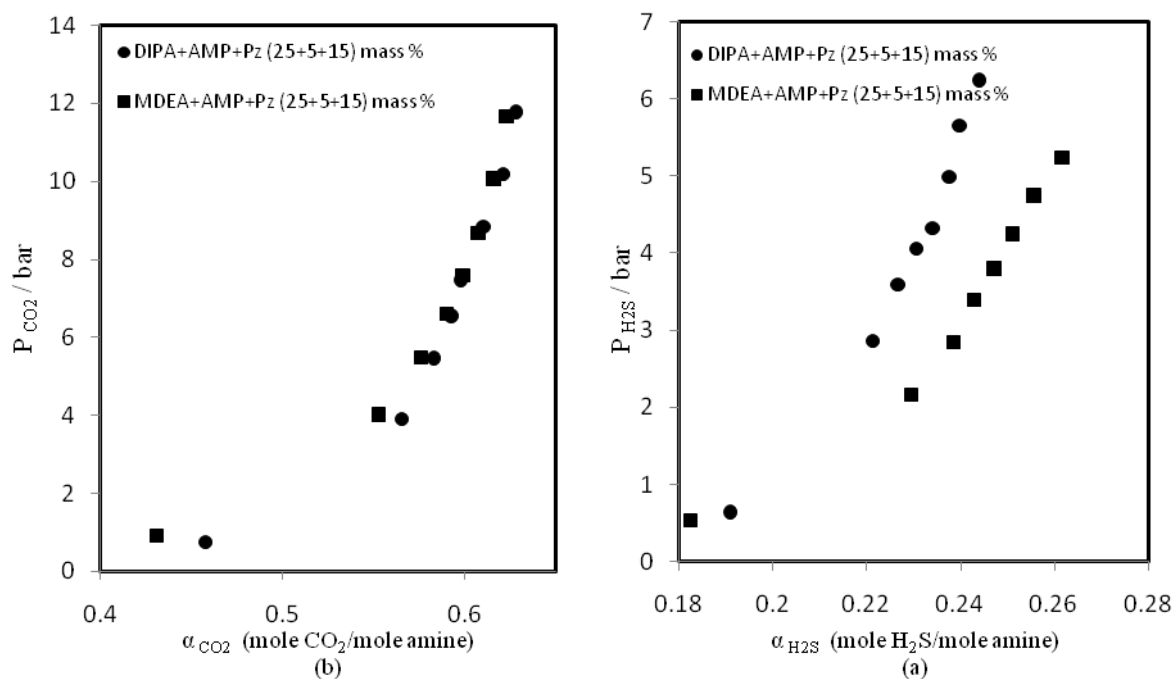


Fig. 9. Comparison between aqueous solutions of MDEA+AMP+Pz (25+5+15) mass % and DIPA+AMP+Pz (25+5+15) mass % to absorb. (a) H₂S in the presence of the CO₂. (b) CO₂ in the presence of the H₂S.

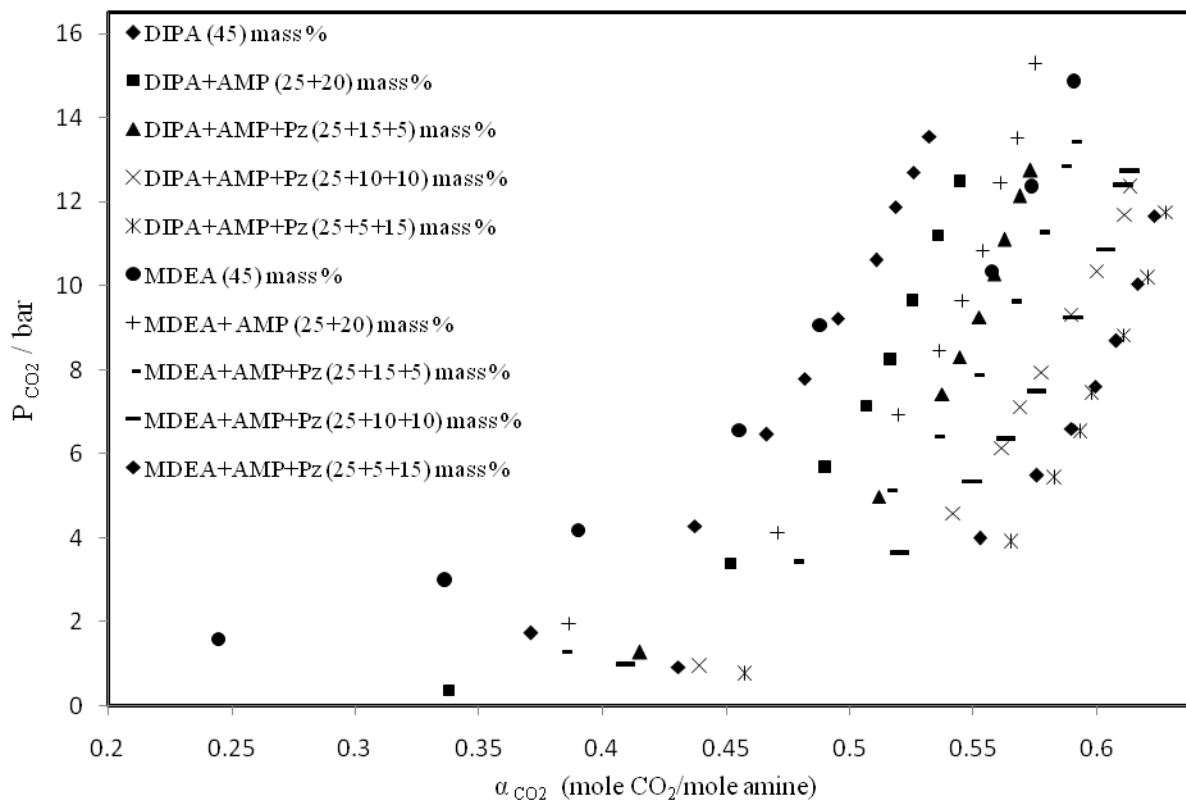


Fig. 10. Partial pressure of the CO₂ versus its loading for solubility of the CO₂ in the presence of the H₂S in all of the aqueous solutions of MDEA-based and DIPA-based.

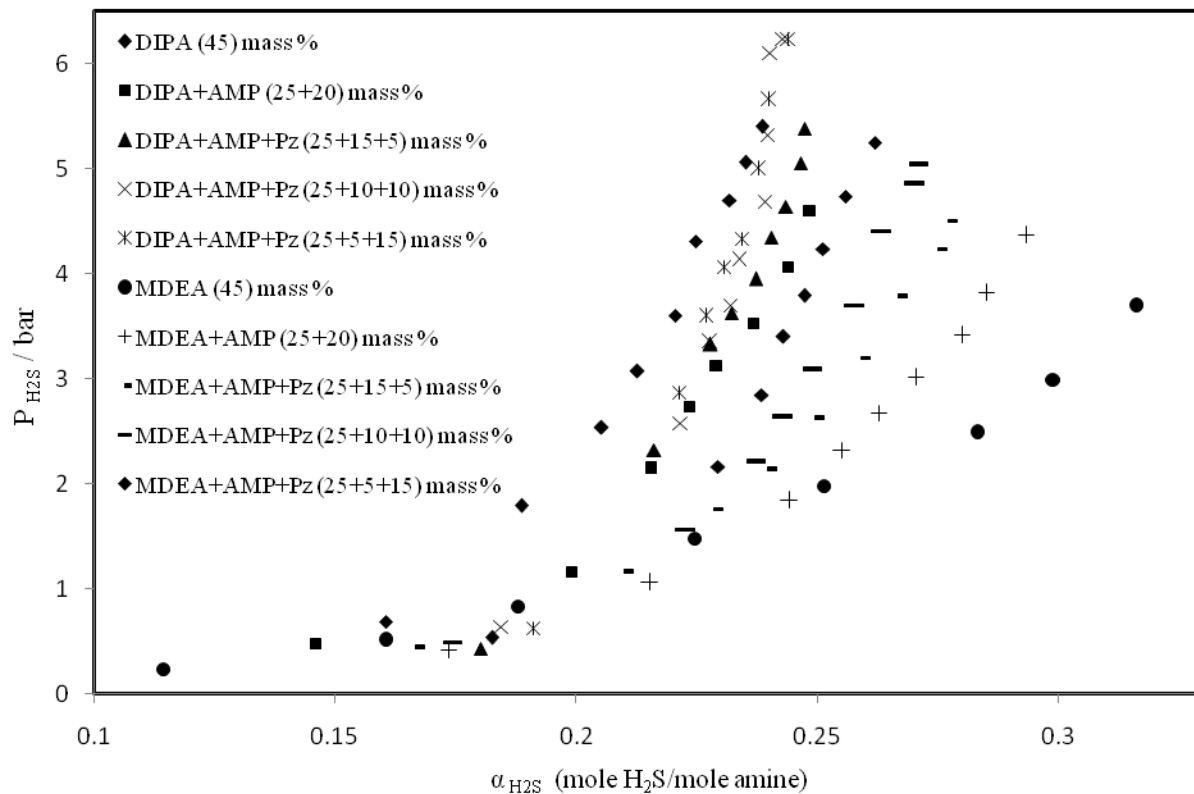


Fig. 11. Partial pressure of the H₂S versus its loading for solubility of the H₂S in the presence of the CO₂ in all of the aqueous solutions of MDEA-based and DIPA-based.

Highlights

- A static equilibrium cell is used for simultaneous measurement of H₂S+CO₂ solubility in alkanolamine blends at high pressure
- The MDEA-Piperazine-AMP and DIPA-Piperazine-AMP systems are investigated
- Piperazine and AMP improves CO₂ solubility and decrease H₂S solubility in both DIPA-based and MDEA-based systems.