



Solubility of Carbon Dioxide in Aqueous Mixture of Aminoethylethanolamine + Sulfolane at High Pressure and Different Temperatures

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Abstract

In recent years, the emission of greenhouse gases especially carbon dioxide has been increased. Since CO₂ is accounted for as a gas pollutant and leads to global warming, the removal of carbon dioxide is an important step in a gas capturing process. In this study, the solubility of carbon dioxide in mixtures of the chemical and physical solvents at different compositions is measured using a static high-pressure equilibrium cell. The measurements are carried out for the two different blends of sulfolane + Aminoethylethanolamine(AEEA) + water with the mass compositions of (20-20-60) wt.%, and (10-20-70) wt.% , respectively, at 313.15 and 328.15 K within the total pressure range of 100 – 5300 kPa. The results show that for both systems at the given composition, by increasing temperature the loading of CO₂ was reduced at a fixed partial pressure of CO₂. In addition by increasing the partial pressure of CO₂ at a fixed temperature, the CO₂ absorption was enhanced. Moreover, the present findings showed that CO₂ solubility was enhanced by increasing either sulfolane or AEEA concentration. However, at low acid gas loading, the CO₂ loading was reduced by enhancing the sulfolane concentration.

Keywords: Carbon dioxide, solubility, 2-(2-Aminoethylamino) ethanol (AEEA), Sulfolane.

Introduction

In natural gas industries, acid gas contaminants such as carbon dioxide, hydrogen sulfide and; sulfur compounds (COS, CS₂, SO₂, and mercaptans) significantly influence the quality of natural gas. Moreover, capturing carbon dioxide in petrochemical industries such as ammonia production, power plants, and oil refineries are necessary to protect the environment. Thus, the removal of unfavorable CO₂ in natural gas treatment units is a major step to improve the heating value of natural gas. Hence, so far the several methods have been developed to remove acid gases from natural gas and numerous researches have been conducted for CO₂ capturing [1]. Among various techniques, chemical absorption of the acid gases through aqueous alkanolamines solution has been the most convenient method in the various industries. The main advantage of the chemical solvents is their capability to remove the acid gases to low levels at low partial pressures. Moreover, their losses are not substantial, since the solvent is water, and hydrocarbons solubility is very low in these solutions. The main disadvantages of using the aqueous alkanolamines are high recovery energy requirement, limited loading and the problem of degradation and corrosion [2]. Hence, a blend of the



chemical with physical solvents allows one to use a suitable absorption solution to overcome this problem. In physical solvents, the absorption is not restricted by the stoichiometry, and the regeneration of the solvent could be done by reduction of the pressure. Besides, the Sulphur compounds such as COS and thiols could be removed by this method [3]. The absorption of CO₂ in a mixture of alkanolamine and physical solvents is a promising technique since this mixture reduces disposable contaminated solvents. Using a mixed solvent allows one to take the advantages of both types of physical and chemical solvents. [4].

Several investigations have carried out to measure the solubility of CO₂ in the various aqueous alkanolamines and a mixture of chemical and physical solvent. Zoghi et al. [5] measured the solubility of CO₂ in an aqueous solution of AEEA (30 wt.%) at 313.2 to 368.2 K through CO₂ partial pressures in the range of atmosphere to 4400 kPa. In another work, Guo et al. [6] reported that the partial pressure of CO₂ versus its loading for the aqueous solutions of AEEA, AEEA + MDEA and AEEA + AMP at 303, 313, and 323 K. They found that by increasing the weight ratio of MDEA to AMP in the aqueous AEEA system led to the reduction of the CO₂ loading, but the absorption rate increased. New experimental vapor-liquid equilibrium data of CO₂ in a hybrid solvent were reported by Bandyopadhyay et al. [7] that were containing sulfolane as a physical solvent along with aqueous (MDEA + PZ) over the temperature range of 308 to 328 K and CO₂ partial pressure range of 1–1400 kPa. Sh. Zhang et al. [8] investigated a novel data of sulfolane hybrid serving as the liquid phase splitting absorbent for CO₂ capture. The absorption kinetics was investigated by a wetted-wall column using 2 M DETA + 3 M sulfolane absorbent for CO₂ uptake. The thermodynamics was studied by revealing the phase splitting behavior and calculating the heat duty at the vapor-liquid equilibria (VLE) mode within the temperature range of 303- 328 K. However, various researches have been needed for acid gas solubility in the aqueous alkanolamines solutions and lack of experimental data at various temperatures, pressure, and concentrations to design and simulate acid gas removal units in acid gas removal and capturing units..

The main objective of this study is to investigate solubility of CO₂ in mixed solvent of AEEA + Sulfolane + water with a combination of (20-20-60) wt.% and (20-10-70) wt.% at temperatures 313.15 and 328.15 K.

Experimental

Materials

Aminoethylethanolamine (AEEA) and sulfolane (TMS) with the molar purity >98% were supplied from Merck. The CO₂ gas cylinder was supplied by Mahan Gas Company with a molar purity of 99.99%. All the materials were used without further purification. A digital balance with an accuracy of ±0.001g was used to weigh the chemicals and water.

Apparatus

The solubility data are obtained through pressure measurement using a quasi-static high-pressure apparatus as shown in Fig.1. The experimental setup consists of an equilibrium cell made of Hastelloy C22/C276 with a capacity of about 285 ml; tolerate pressure up to 350 bar and temperature up to 300 °C. The cell is equipped with a magnetic stirrer for agitation of the liquid phase. A 316 stainless steel storage tank with capacity about 245 ml that is used for injection of the acid gases into the equilibrium cell. The gas cylinders connect to the storage cell and a precise thermostatic circulator is used to keep the cell isothermally at a given temperature. The temperature and pressure of the gas-liquid equilibrium sample were measured in the cell, respectively, by a platinum temperature sensor (PT-100) and the 0–100



bar calibrated pressure transducer (model 33X, Keller, Switzerland) with an accuracy of $\pm 0.0175\%$ of full scale. For the injection cell, a calibrated thermocouple thermometer (model ST-612, Standard Instrument Co. Ltd., Hong Kong) with an accuracy of ± 0.1 K and (0–100) bar calibrated pressure transducer (model 33X, Keller, Switzerland) with an accuracy of $\pm 0.017\%$ of full scale were used. The vapor pressure of the aqueous alkanolamines systems was measured through a 0–1 bar pressure transducer (model PTF106, Indumart, Canada) with an accuracy of $\pm 0.3\%$ of full scale. The temperature of the equilibrium cell was controlled within ± 0.01 K using a highly responsive circulator temperature controller (unistat tango nuevo, Büchi AG, Switzerland). The cell is evacuated using a vacuum pump (model DV-142N-PLATINUM 5 CFM, JB company, USA and a monitoring unit (bds mc, Büchi AG, Switzerland) and a personal computer is used for receiving and storing all of the data from the measurement devices

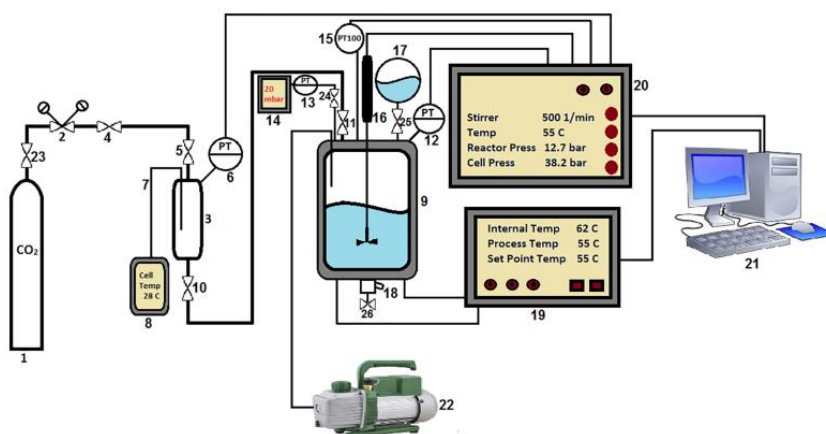


Fig 1. Scheme of gas solubility measuring apparatus in alkanolamine: (1) CO₂ cylinder, (2) regulator, (3) injection cell, (4,5,10,11,23–26) valves, (6,12,13) pressure transducers, (7) thermocouple thermometer, (8) temperature monitoring, (9) equilibrium cell, (14) pressure monitoring, (15) temperature sensor, (16) stirrer, (17) solution reservoir, (18) drain valve, (19) thermostatic circulator, (20) monitoring unit, (21) PC, (22) pump [9]

Experimental procedure

In this work, deionized water was used to prepare the solutions. By using a vacuum pump, gases were evacuated from the equilibrium cell. Almost 90 g of the fresh mixture of (AEEA + sulfolane + water) was fed into the equilibrium cell. The temperature of the equilibrium cell was set to the desired temperature by means of a thermostatic circulator and the solution was at equilibrium with its own vapor pressure (P_v). The vapor pressure of the solvent was recorded by the (0 to 1) bar absolute pressure transducer. A known amount of CO₂ (n_{CO_2}) introduced to the equilibrium cell and its number of moles is calculated as

$$n_{CO_2} = \frac{V_{gs}}{R} \left(\frac{P_{gs1}}{T_{gs1} Z_1} - \frac{P_{gs2}}{T_{gs2} Z_2} \right) \quad (1)$$

where V_{gs} is the volume of the gas storage vessel, Z_1 and Z_2 are the compressibility factors, respectively, corresponding to the initial condition of pressure and temperature (T_{gs1} , P_{gs1}), and the final condition (T_{gs2} , P_{gs2}) of the gas-storage vessel for each gas injection step to the equilibrium cell. Both compressibility factors are calculated through a suitable cubic equation of state (Peng–Robinson EOS). Then, the stirrer was switched on at a constant speed during the experiment so that the equilibrium was attained when the pressure of the equilibrium cell (P_{tot}) presents no change for about 30 min. Therefore, the partial pressure of solvent is



assumed to be equal to the vapor pressure of the solvent at various measuring pressures and thus, the equilibrium partial pressure of CO₂ (P_{CO₂}) is calculated as

$$P_{\text{CO}_2} = P_{\text{tot}} - P_v \quad (2)$$

The number moles of CO₂ that were remaining in the vapor phase at the equilibrium condition is given as:

$$n_{\text{g,CO}_2} = \frac{V_g P_{\text{CO}_2}}{ZRT} \quad (3)$$

where V_g and Z_{CO₂} are the volume and compressibility factor of CO₂ in the vapor phase of the equilibrium cell, respectively, and T is the temperature of the equilibrium cell. The volume of the vapor phase was calculated by the difference of the equilibrium cell volume and the volume of the aqueous solution that is calculated using the density of the solution at experimental temperature. It should be noted that the liquid phase is assumed to be incompressible. Finally, The CO₂ loading in the liquid phase is defined as α and mole fraction x_{CO₂} as follows:

$$\alpha_{\text{CO}_2} = \frac{n_{\text{CO}_2} - n_{\text{g,CO}_2}}{n_{\text{AEEA}}} \quad (4)$$

$$x_{\text{CO}_2} = \frac{n_{\text{CO}_2} - n_{\text{g,CO}_2}}{n_{\text{AEEA}} + n_{\text{H}_2\text{O}} + n_{\text{sulfolane}} + (n_{\text{CO}_2} - n_{\text{g,CO}_2})} \quad (5)$$

Results and discussion

Validation test

To validate the present apparatus and the experimental procedure, the solubility of CO₂ into an aqueous solution of AEEA (30 wt. %) was measured at 328.15 K and pressure range of about 70 to 4000 kPa. The results are compared with those obtained by F. Feyzi et al. [5] as shown in Fig. 2. The present data are in good agreement with the literature data that demonstrate the validity and the accuracy of the present measurements and the experimental procedure.

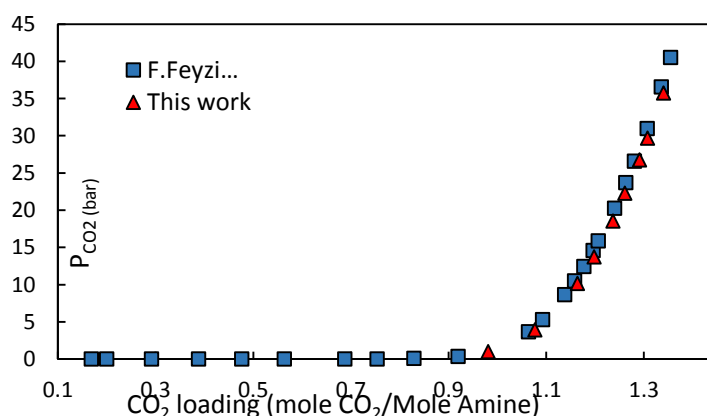


Fig 2. Comparison of experimental results from the present work and the literature for the solubility of CO₂ in the aqueous solution of water (70 wt. %) and AEEA (30 wt. %) at 328.15 K. F.Feyzi et al.[5]: (■), This work: (▲)

Solubility measurement

In this work, the experimental data of the solubility of CO₂ in two different blends of Aminoethylethanolamine (AEEA) +sulfolane + water with the mass compositions of (20-20-60) wt.% and (20-10-70) wt.% , respectively, were obtained at 313.15 and 328.15 K and



within the pressure range of 100 to 5300 kPa. Figure 3 presents the data of the partial pressure of CO₂ versus its loading at the various compositions and temperatures.

The results show that for the aqueous sulfolane + AEEA system at the given composition, by increasing temperature the mole fraction of CO₂ was reduced at a fixed partial pressure of CO₂ and the fixed temperature, by increasing the partial pressure of CO₂, the CO₂ absorption was enhanced.

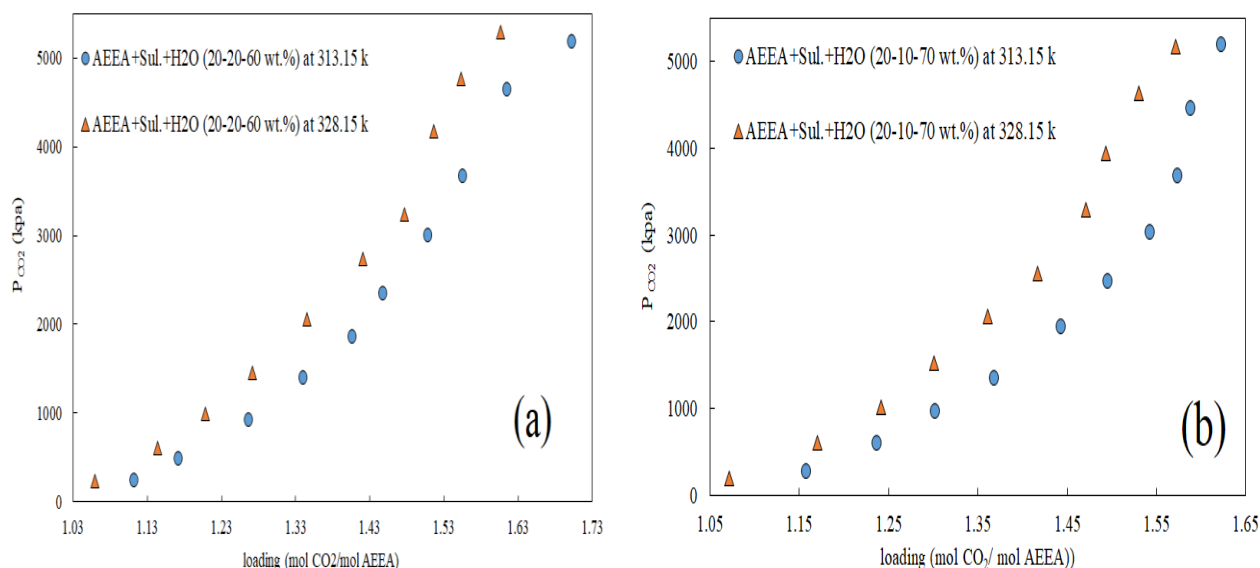


Fig 3. The CO₂ partial pressure versus its loading in an aqueous solution at 313.15 and 328.15 K (a) AEEA+Sulfolane+H₂O (20-20-60) wt.% (b) AEEA+Sulfolane+H₂O (20-10-70) wt.%

Figure 4 presents the data of the partial pressure of CO₂ versus its loading at the various compositions and isothermal condition. The present findings showed that CO₂ solubility was enhanced by increasing either sulfolane or AEEA concentration. However, at low acid gas loading, the CO₂ loading was reduced by enhancing the sulfolane concentration.

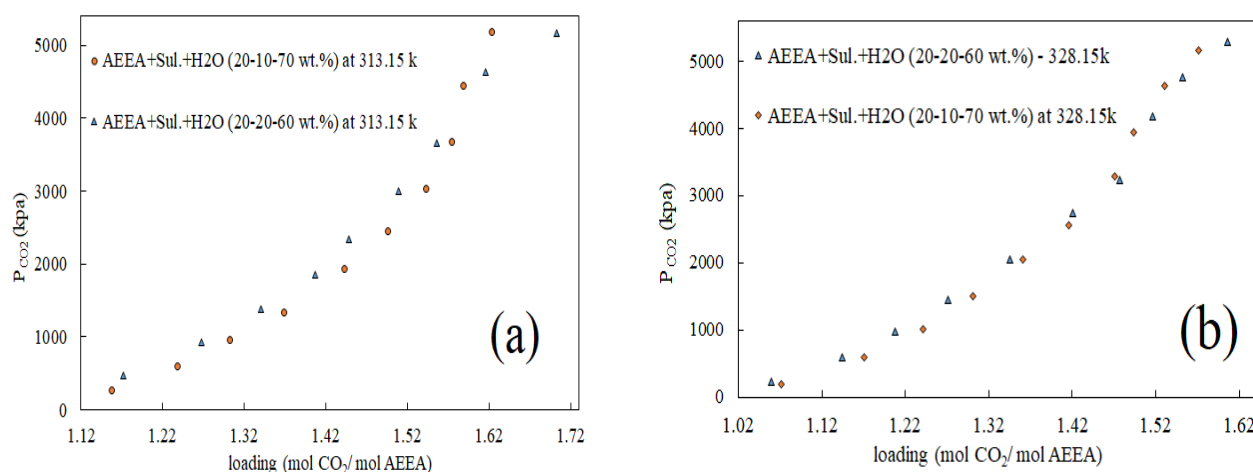


Fig 4. The CO₂ partial pressure versus its loading in an aqueous solution of AEEA+Sulfolane+H₂O (20-20-60) wt. and of AEEA+Sulfolane+H₂O (20-10-70) wt.% at (a) 313.15 and (b) 328.15 K.

Conclusions

In this study, the solubility of CO₂ into the aqueous solutions of sulfolane + AEEA was measured at 313.15 and 328.15 K and in the total pressures of 100 – 5300 kPa by using a



static high-pressure equilibrium cell through a volumetric method. The prepared mass fractions of solvent mixtures of AEEA+Sulfolane+H₂O were (20-20-60) wt.% and (20-10-70) wt %. The solubility data were tabulated in forms of the acid gas partial pressures against its loading (mole CO₂/mole AEEA). The influence of temperature and pressure on the solubility of CO₂ into each solvent mixture were presented. As observed, the loading of CO₂ enhanced with the reduction of temperature or increasing partial pressure. Moreover, the present findings showed that CO₂ solubility was enhanced by increasing either sulfolane or AEEA concentration. However, at gas loading of 1.57 at 313.15 K for the first system and for loading 1.45 at 328.15 K for the second system the CO₂ loading was reduced by enhancing the sulfolane concentration.

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