

Real Acid Natural Gas Solubility Measurement in Novel Hybrid Solvents of Amine and Ionic Liquids

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ABSTRACT: This study aims to investigate the performance of various hybrid solvents of amine and ionic liquids in the acid gas sweetening process. Two ionic liquids including [Hmim][NO₃] and [Bmim][Ac] were used with MDEA amine solvent to investigate the solubility of H₂S, CO₂, and various hydrocarbons from a real natural gas. The solubility data were measured at a pressure range of 2–44 bar, temperature range of 298.15, to 338.15K and ILs loading of 10–20(wt.%) in the hybrid solvents. The experimental design was employed to obtain the optimum condition of hybrid solvents. The results show that increasing ILs loading up to 10% in the hybrid solvent increased the CO₂ solubility for both ILs up to 8.6%, and reduced the H₂S solubility by up to 6% at the highest pressure and lowest temperature tested. The effect of pressure is the dominating factor on the solubility of the acid gases while the temperature and ILs loading percentage play a major role on the solubility of acid gases. In addition, the hybrid solvent containing 10 (wt.%) of [Bmim][Ac] showed better solubility towards CO₂ in comparison to the solvents containing [Hmim][NO₃]. It was concluded that this hybrid solvent is more suitable for CO₂ absorption from natural gases containing higher CO₂ and lower H₂S concentration.

KEYWORD: Solubility, hybrid solvent, Ionic liquids, amine solvent, Natural gas.

INTRODUCTION

Natural Gas is one of the main sources of energy in domestic and industrial applications, which is inexpensive and nearly non-contaminant. Petroleum-derived gases contain hydrogen sulfide and carbon dioxide in different amounts depending on the origin of the crude oil or natural gas reservoir. H₂S presented in natural gas, is a harmful and dangerous gas that threaten health, increase corrosion in gas pipeline and also, release SO₂ into the atmosphere during combustion of natural gas. CO₂ presence in the natural gas reduces the heating value of the gas, causing severe corrosion and the formation of hydrate in gas

pipelines for gas transmission. Therefore, it is evident that removal of these compounds (H₂S and CO₂) in gas processing is a necessity[1].

Various processes for the separation of CO₂ and H₂S (acid gases) have been developed, such as adsorption by solid adsorbents, absorption by solvents, membrane and cryogenic separation [2–6]. However, the choice of selecting various sweetening processes is governed by the level of impurities that are presented in the sure gas. Among various methods for acid gas sweetening, absorption with physical and chemical solvents has

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widespread use at the industrial scale. This process removes acid gas impurities such as H₂S, CO₂ and various mercaptans from natural gas. The temperature and pressure of the process are usually in the range of 300~350 K and pressure of up to 80 bar, respectively [7].

In absorption separation technologies, the absorption mechanism is classified based on the intermolecular bond formation during the processes. Based on this classification, the physical and chemical absorption process is introduced [8]. Where, in the physical process, weak intermolecular forces are responsible for the absorption of the contaminant in the liquid phase, and it's highly affected by the partial pressure of the contaminant in the gas phase. While, in chemical absorption, strong intermolecular forces come into play, and a chemical reaction occurs between contaminant acid gases and the solvent molecules [9].

Many commercial physical and chemical solvents for natural gas sweetening (removal of acid gases) are available [10]. For example, Selexol (Polyethylene glycol and dimethyl ether mixture) and Rectisol (methanol solvent) are widely used physical solvents, while monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), and promoted methyl diethanolamine (promoted MDEA with piperazine) are common chemical solvents for gas sweetening [11]. Absorption by alkanol amine solutions is one of the oldest and most widely used technology for the separation of H₂S and CO₂ from natural gas [12]. Primary amines (such as MEA) have a high absorption rate but lower capacity toward acid gas and secondary amines (such as DEA) have a higher capacity but lower absorption rate compared to primary amines. While tertiary amines such as MDEA have higher capacity compared to the other two amine types, their absorption rates are lower [13–15]. This limitation is overcome by the addition of primary or secondary amines (MEA, DEA, PZ) as an activator to MDEA [16].

However, these mixtures of amines have a high tendency to degrade in the regeneration process where the absorbed acid gas is removed from the solvent, and also is highly corrosive in presence of water. To reduce these drawbacks, the hybrid solvent concept has been introduced recently, where ionic liquids as green solvents are combined with amine solvents to enhance the absorption rate and reduce the energy requirement of the regeneration at the same time [17].

Ionic liquids are a new class of solvents with unique features such as low vapor pressure, thermally stable, and high physical solubility of acid gases [18]. Currently, Ionic liquids are more expensive than conventional solvents. Therefore, they are not economically affordable. Despite higher cost of ionic solvents, they are promising solvents for gas sweetening process [19].

Various studies can be found in the literature regarding hybrid solvents, including amines and different ionic liquids, for gas sweetening or CO₂ capture processes [20–22]. Research shows that a mixture of IL and aqueous amine solution can reach up to 90% of its capacity in less than 15 min, and complete chemisorption achieved after 25 min. Therefore, it is a viable option to blend ILs with other amines to achieve maximum acid gas absorption capacity, faster absorption rates and reduce the overall energy requirement of the process [10,21,23,24].

From many ILs that was investigated for acid gas treatment, imidazolium based ionic liquids showed higher affinity toward CO₂ which is miscible in water and MDEA [25–27].

So many research have been conducted to evaluate hybrid solvents of amines and ILs performance [21]. However, finding the best hybrid solvents that can be utilized commercially, requires more investigation in this field. To the best of our knowledge, all the studies that employed ILs as hybrid solvents with amines used pure acid gases, which has higher partial pressure compared to real natural gas. The higher partial pressure of acid gas in the absorption process leads to higher solubility value compared to the real case due to the elimination of mass transfer resistance. Therefore, it is necessary to measure the solubility of acid gases by any solvent in the real natural gas. In this way, the performance of a solvent can be evaluated based on actual conditions.

This work aims to investigate the aqueous solutions of methyldiethanolamine + [Bmim][Acetate] and methyldiethanolamine + [Hmim][NO₃] hybrid mixtures for absorption of acid gases, including (H₂S and CO₂) in real natural gas. In a well-designed experimental setup, the solubility of acid gases was measured experimentally at different temperatures and pressures. The effects of temperature and loading percentage of ionic liquids in an aqueous hybrid mixture was investigated. An experimental design procedure was employed to obtain the optimum conditions for formulated hybrid solvents.

MATERIAL AND METHODS

Materials

The chemicals used in this study include: methyldiethanolamine (MDEA), which is purchased from ACROS Co., 1-butyl-3-methylimidazolium acetate ([Bmim][Ac]) provided from sigma, 1-Hexyl-3-methylimidazolium Nitrate ([Hmim][NO₃]) was purchased from a local chemical company called ATLAS SHIMI SABZ in Iran and deionized water provided from RAMIN power plant in Ahvaz, Iran. In order to remove water and other volatile compounds from ionic liquids, all ILs was stirred at a high temperature (70 °C for 20h) under high vacuum.

The gas sample used in this study was a real natural gas from the Bidboland gas refinery in Khozestan province in Iran. The received gas samples from the refinery was analyzed by three different gas chromatograph devices with different columns installed on them. The composition of the gas measured with accuracy of ±0.1 mol.%. The natural gas sample contains methane (86.59%), ethane (5.83%), propane (2.57%), i-butane (0.45%), n-butane (0.81%), i-pentane (0.31%), n-pentane (0.32%), i-hexane (0.18%), n-hexane (0.12%), i-heptane (0.036%), n-heptane (0.03%), H₂S (0.025%), N₂ (0.21%) .CO₂ (2.52%). The details of all utilized chemicals and gas mixture are presented in Table 1.

The water content of the ILs was measured by the Karl Fischer device (Mettler DL38 Volumetric KF Titrator). The HPLC analysis of heated ILs under high vacuum shows that the impurities from solvents were removed. The density of the [Bmim][Ac], [Hmim][NO₃] and amine solvent was reported as 1.0526 [29] and 1.1175 g/cm³ [30] and 1.038 g/cm³, respectively. Both of these ILs have good miscibility in water and various physical properties of these materials reported in the literature.

Experimental Apparatus and Procedure

In this study, the same experimental apparatus that employed by *Shaahmadi et.al* [31] was used in order to measure the gas solubility in hybrid solvents of ILs + amines. All tests were conducted at three temperatures, including 298.15, 318.15 and 338.15 K in pressure range of 2 to 44 bars. In summary, the experimental setup consists of a vessel as a gas feeder, a series of opening and closing valves, an absorption cell with a circulating water jacket to control temperature, a water bath to set the

circulating water temperature, a series of pressure transmitter for recording the pressure change in both gas feed vessel and in the absorption cell, a data logger which collects and log all relevant data and finally a gas chromatograph device for measuring gaseous components. The schematic of the experimental setup is presented in our previous work [32]. In order to validate the setup accuracy, the data from *Shaahmadi et al.* was reproduced in this setup and the uncertainty of three different runs for the mole fraction of a pure CO₂ gas was about ±0.0001. Three standard gases were used to calibrate the GC device and the pooled standard deviation was calculated for each component. For CO₂ mole fraction, the pooled standard deviation was ±0.00019 and for methane, it was measured ±0.00112.

In a typical test, a known mass of hybrid solvent was placed into the equilibrium cell, and then the entire system was evacuated by a vacuum pump. The cell temperature is set to the desired value by a circulator. Afterwards, a known amount of gas was introduced into the equilibrium cell (the volume of each section of the setup is known). The amount of gas injected into the cell was calculates as follow:

$$n_{gas} = \frac{V}{RT} \left(\frac{P_i}{Z_i} - \frac{P_f}{Z_f} \right) \quad (1)$$

where, V is the volume of the gas container, T is the temperature of the gas and R is the universal gas constant. P_i and P_f are the initial and final pressures. Z_i and Z_f are the compressibility factors for the initial and final pressures and temperature of the gas container, respectively. After contacting hybrid solvent with natural gas, the equilibrium condition achieved when the pressure change in the system becomes constant over time (P_{equil}). The moles of acid gases, including CO₂ and H₂S, remained in the gas phase was obtained by using an appropriate equation of state at P_{equil}, T of the cell, and volume of the system. The moles of acid gases in the liquid phase n_{l,gas} will be determined from:

$$n_{l,gas} = n_{gas} - n_{g,gas} \quad (2)$$

The gas chromatograph used for gas analysis was an Agilent 7890 device, which was equipped with a FPD, a TCD and a FID detector for analysis of H₂S, CO₂, and hydrocarbon concentrations, respectively. Three standard gas were used for calibration of each detector and respective column. The GC column for the FPD was a Silica PLOT capillary column 30m x 0.32mm, film

Table 1: The Details of Materials and Gas Mixture Used in this Study

Chemical Name	Chemical formula	CAS No.	Purity (as purchased)	Water content (after dehydration)	Molecular Weight	Purification method
1-Butyl-3-methylimidazolium acetate (BMIM)(Ac)	C ₁₀ H ₁₈ N ₂ O ₂	284049-75-8	≥96.0% HPLC	<50 ppm	198.26	Supplier data
1-Hexyl-3-methylimidazolium Nitrate (HMIM)(NO ₃)	C ₁₀ H ₁₉ N ₃ O ₃	203389-26-8	≥96.0% HPLC	< 50 ppm	229.28	Supplier data
Methyl diethanolamine(MDEA)	C ₅ H ₁₃ NO ₂	105-59-9	>99% (m)	<50 ppm	119.16	Supplier data
Natural gas	Filled pressure= 120 bar	-	GC analyzed	-		Analyzed by GC

thickness 4 μm. The channel of FPD detector on GC for H₂S measurement was calibrated for two ranges of low level and high level.

Experimental Design

In this study, two different ILs were used with a single amine solution. The percent of ILs in the mixture solvent, temperature and pressure was considered effective parameters on the solubility. In a separate work, the authors investigated the effect of pressure and temperature on natural gas solubility in ILs [32]. The aim of this study is to find an optimum IL percent in a hybrid mixture in order to maximize the solubility of CO₂/H₂S in comparison to amine solvent alone. Therefore, an experimental design procedure was employed to reduce the experimental efforts. The response surface methodology was used with three numerical parameters (pressure, temperature and IL concentration in hybrid solvent) and one categorical parameter (type of IL). The D-optimal (custom design) as a flexible design structure to accommodate custom models, categorical factors, and irregular (constrained) regions was used for the design matrix. The design matrix included 40 experiments. The results are presented in the following section.

RESULT AND DISCUSSION

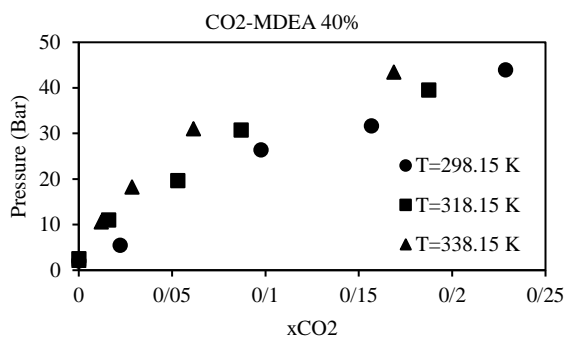
The Solubility of CO₂ in Hybrid Solvents

The experimental solubility of CO₂ in the hybrid mixtures of [Bmim][Ac] and [Hmin][NO₃] with MDEA amine at different mixture percentages are presented in Fig. 1.

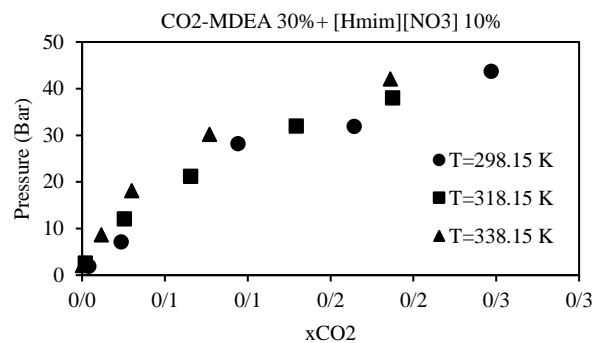
In this study, the MDEA solution was selected as a benchmark. As can be seen from Fig. 1, the solubility of CO₂ is directly affected by pressure and temperature, as with increasing the pressure, the solubility is also increased in all pure and hybrid solvents, while with increasing the temperature, the solubility is reduced in all solvents as

expected. However, increasing the ILs percentage up to 10% in the hybrid solvent, the CO₂ solubility increased from 0.23 for MDEA solvent at 43.9 bar to 0.247 at 43.7 bar for [Hmim][NO₃], which is about 6.3% increase in the solubility. As for [Bmim][Ac], the solubility for CO₂ at 10% ILs+ MDEA increased to 0.254 at the same pressure, which is about 8.7% increment. By increasing the IL loading percentage from 10% to 20%, the solubility of CO₂ for both ILs decreased. The results indicate that lower IL loading favors the absorption of CO₂. This finding is in agreement with the results that were previously reported by *Hailegiorgis et al.* [33]. Comparing these findings with the results of pure solubility of ILs, including our previous work [32], it can be seen that the hybrid solvent is only effective at low IL loading in the MDEA in the case of [Bmim][Ac] for CO₂ absorption [34–36]. Increasing IL loading in the hybrid solvent reduced the amount of solubility by up to 25%. It was expected that when ILs are added to the MDEA, the solubility would not reduce because of the high affinity of ILs towards CO₂ absorption. One reason for this reduction in the solubility can be attributed to the difference in the nature of absorption by amine and ILs. The absorption of CO₂ by amine is of a chemical nature, which highly depends on the kinetic parameters of the system. While, the CO₂ absorption by ILs, is mainly physisorption and it is a slower mechanism. Also, the new findings suggest that CO₂ can go under a chemical reaction in [Bmim][Ac] as it was shown by *Cui et al.* [37]. But probably the kinetic of CO₂ absorption by amine is faster than the IL reaction and it is the dominant step in the whole absorption process.

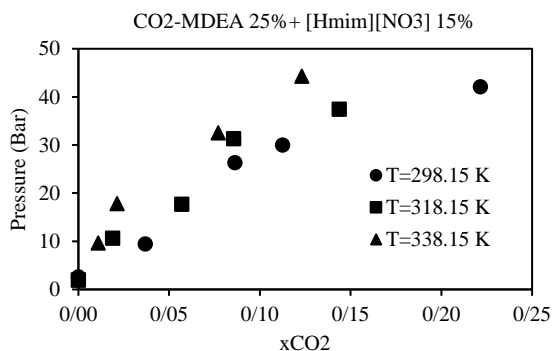
On the other hand, increasing the amount of ILs in the hybrid solvent can increase mass transfer resistance on the interface and within the solvent phase, which can reduce the amount of absorption. Another reason for the reduction in the solubility is that during CO₂ absorption by hybrid solvent, absorption of CO₂ in the solvent phase by either



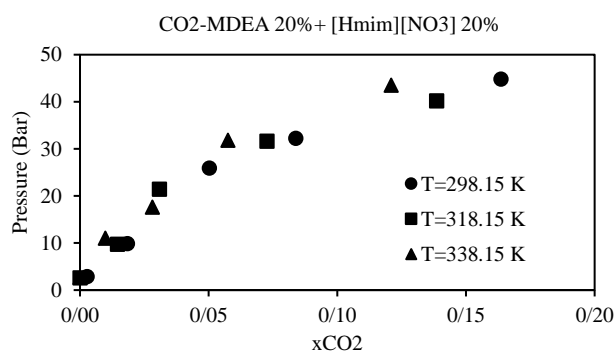
(a)



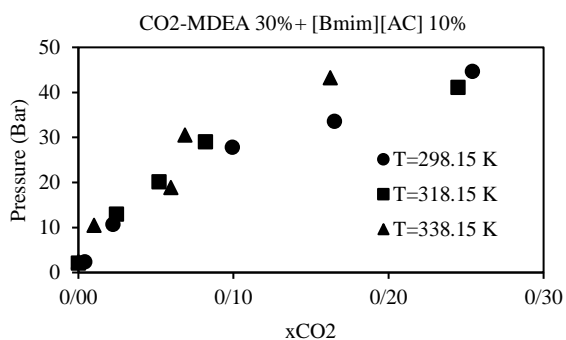
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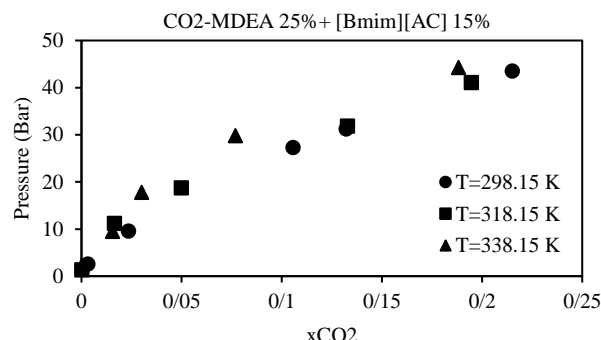
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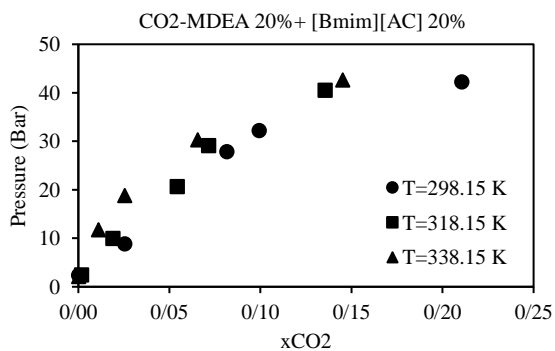
(d)



(e)



(f)



(g)

Fig. 1: The CO₂ Solubility in Amine Solution and Hybrid ILs+ Amine Solution

MDEA or IL absorption can saturate the solvent at lower CO₂ concentration, which can reduce the loading capacity of the solvent [25,38].

Another noteworthy finding of the Fig. 1 is that increasing temperature of the hybrid solvents, can cause more reduction in the solubility of acid gas, where by increasing temperature from 298.15 to 338.15K at 44 bar, the solubility for MDEA solvent reduced by up to 0.056 and 0.061 for 10% ILs hybrid solvent.

The Solubility of H₂S in Hybrid Solvents

The experimental solubility of H₂S in a hybrid mixture of [Bmim][Ac] and [Hmim][NO₃] at different mixture percentages are presented in Fig. 2.

As can be seen from Fig. 2(a-g), the MDEA solvent added as the benchmark for the hybrid solvent comparison. The effect of pressure and temperature on the solubility is the same as for CO₂. However, the results indicate that adding ILs to the amine solution at all percentages reduced the solubility of H₂S in the hybrid solvent. Increasing [Hmim][NO₃] loading from 10% to 20% reduced H₂S solubility from 0.01954 to 0.01835 which is about 6% reduction at pressure of 44 bar and temperature of 298.15K. Also, increasing [Bmim][Ac] to 10% reduced H₂S solubility by about 3% at pressure of 44 bar and temperature of 298.15 K. The same trend was observed for other pressures and temperatures. Comparing the performance of two ILs in this study, shows that the [Bmim][Ac] has a lower negative effect on the H₂S solubility compared to [Hmim][NO₃]. It is evident that, addition of ILs to the amine solvent at lower percentage loading can increase the solubility of acid gases. One can argue that the addition of ILs to amine solvents had adverse effects on acid gas absorption capacity, but the reasons that many literatures tried to combine ionic liquids with amine solvent is other benefits as stated above. Therefore, it can be said that at low ILs percentage loading in hybrid solvent, one can use the benefits of ILs in the hybrid solvent without sacrificing acid gas loading of the solvent. Another reason for reduction in the H₂S solubility can be attributed to the fact that the absorption of CO₂ in the solvent can change the acidity of the solution, which can reduce the amount of H₂S solubility. On the other hand, the physical nature of ILs absorption of acid gases is slower in comparison

to the chemical mechanism of amine solvent absorption. The reduction in amine percentage, which is replaced by ILs, cause a reduction in the H₂S solubility. Because the ILs that replaced the amine can not make up the amount of absorption that would happen with the corresponding amine. The value of solubility of H₂S in the hybrid solvent indicates that the amount of ILs must be tuned to obtain the best results in term of solubility and advantages of ILs in the chemical absorption process.

It is also worth noting that the effect of pressure on solubility reduction of H₂S is less pronounced than that of pure MDEA solvent, where the solubility reduction from 298.15 to 338.15K for MDEA is about 35% and for [Hmim][NO₃] is less than 30% at 10% ILs loading. In contrast for [Bmim][Ac], the solubility reduction at 10% IL loading is more than 41%. It can be concluded that the effect of temperature on the H₂S solubility of [Bmim][Ac] is more pronounced compared to [Hmim][NO₃], but still, the H₂S loading of [Bmim][Ac] stays above the solubility of [Hmim][NO₃] at the same pressure and temperature condition.

Hydrocarbon Solubility in Hybrid Solvents

In this study, the natural gas mixture used for the solubility data measurement. The experimental solubility was measured for all hydrocarbons, but due to the high number of experimental data, only the solubility of methane presented here. The solubility of other hydrocarbons are reported in the supporting information table (TS-1). The experimental solubility of methane in amine and hybrid solvent is shown in Fig. 3(a-g).

The results in Fig. 3 show different solubility of hydrocarbons (methane in this case) in solvent phase by the addition of ionic liquids to the amine solvent. For [Hmim][NO₃], by increasing the ILs percentage from 10 to 20%, the solubility of methane decreased in the hybrid solvent. As for [Bmim][Ac] the solubility of methane at 10% IL+amine solvent is near the pure MDEA solubility, but as increasing the ILs loading in the hybrid solvent, the solubility of methane slightly increased. From these experiments, one can conclude that low loading of [Bmim][Ac] required for the hybrid solvent. However, other parameters of the absorption process, including temperature and pressure must be investigated as well. Finding an optimum value for the ILs loading, pressure and temperature is the next step in this study.

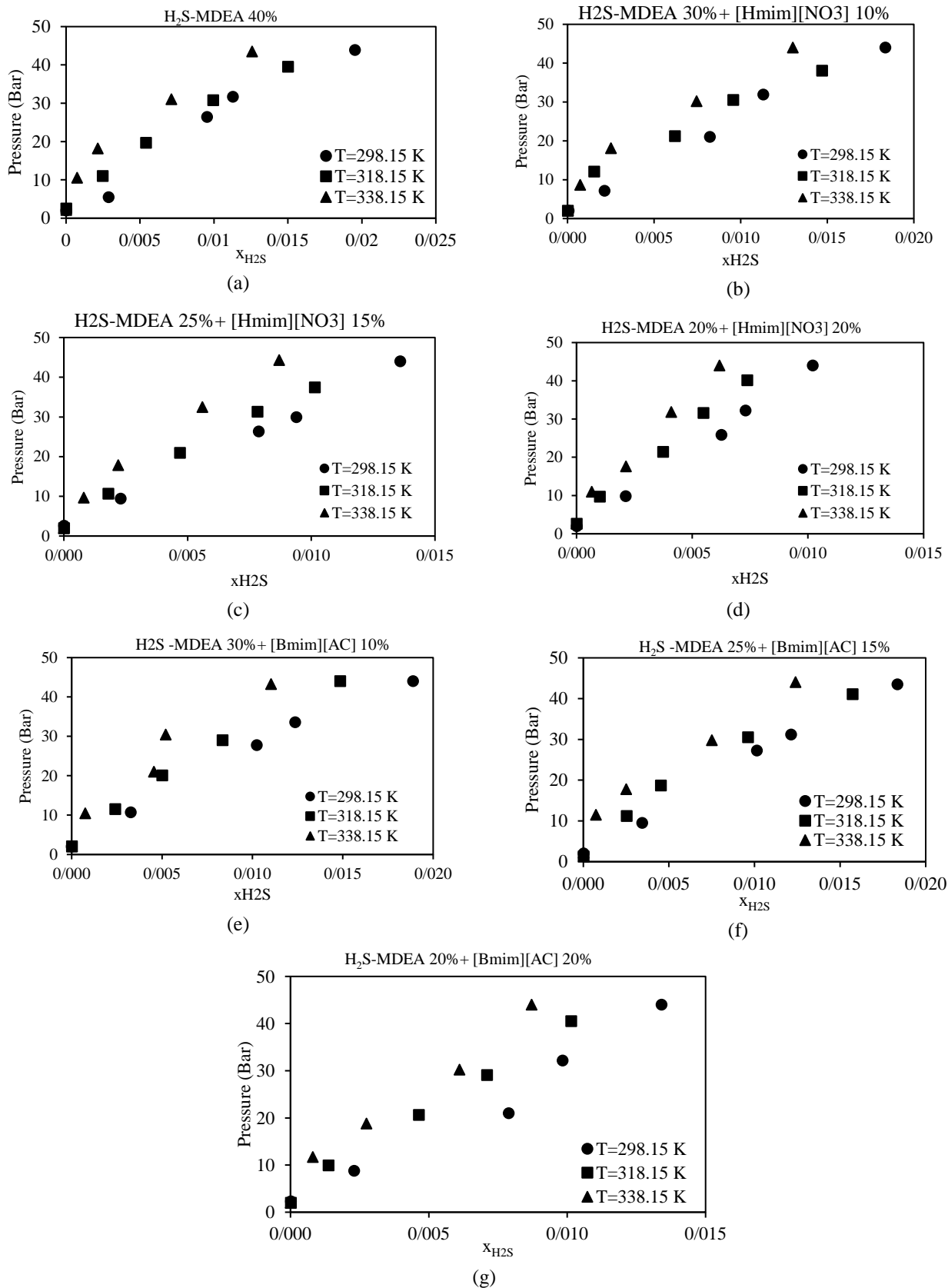


Fig. 1: The H₂S Solubility in Amine Solution and Hybrid ILs+ Amine Solution

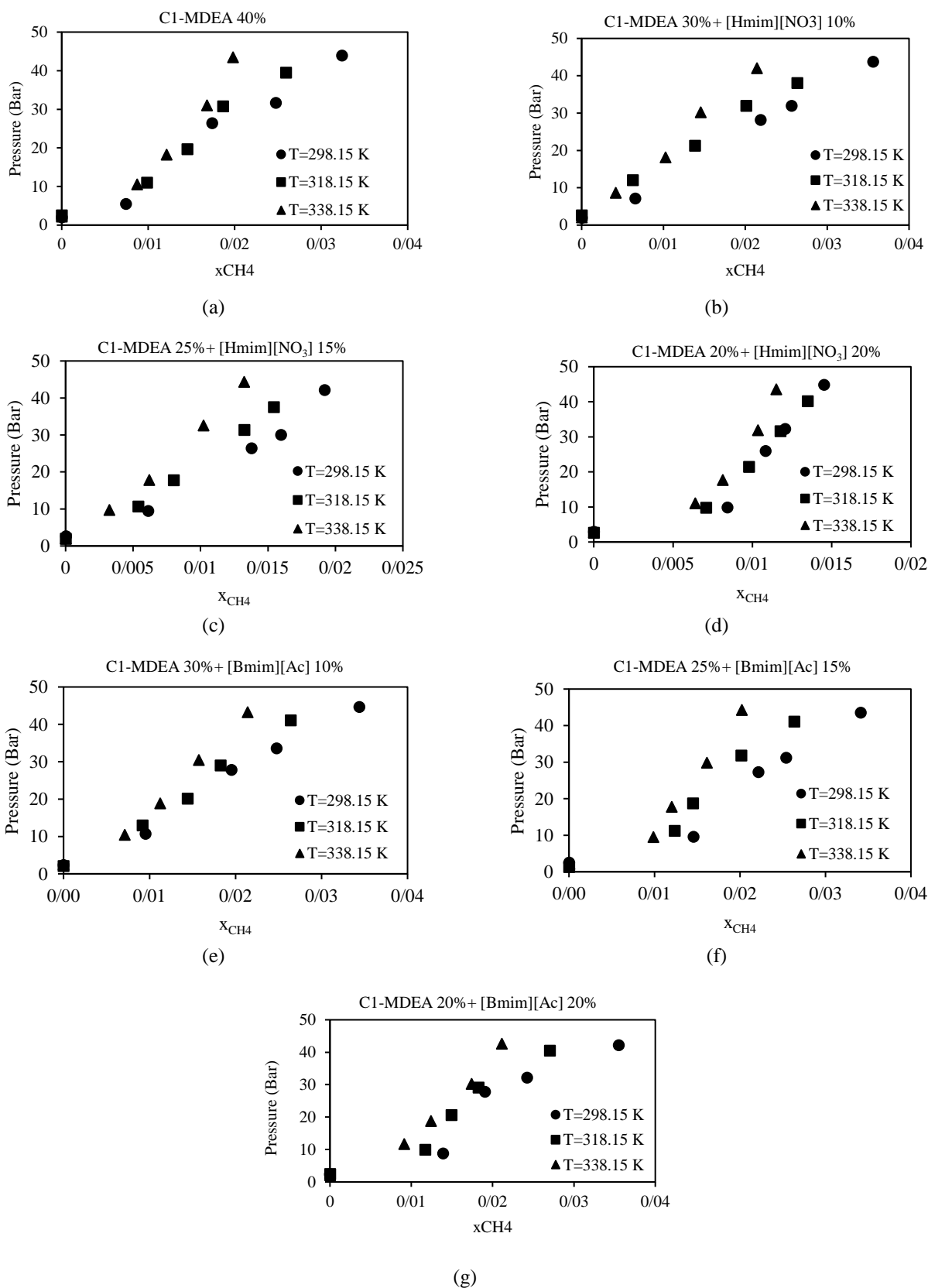


Fig. 2: The Methane Solubility in Amine and Hybrid ILs+ Amine Solvent

Experimental Design Results

The results indicate that increasing IL percentage in the hybrid solvent hurts its performance. On the other hand, the temperature and the pressure of the absorption process is critical to maximize the process efficiency toward higher acid gas loading. The experimental design employed to find the optimum amount of ILs percentage to maximize the CO₂ and H₂S loading in the solvent as well as optimum temperature and pressure conditions for different hybrid solvents. The design matrix consists of four factors, including three numerical factors plus one categorical factor, and two responses, including H₂S and CO₂ concentration in the solvent phase. The design matrix with response variables are presented in Table 2.

As it is shown in Table 2, the solubility measured for CO₂ and H₂S was reported as response variables. The design matrix was analyzed and a quadratic model was suggested. The results of ANOVA for CO₂ presented in Table 3. It should be noted that no transformation function for the data was used for CO₂.

As it can be seen, the model F-value of 99.07 implies that the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate that model terms are significant. In this case, A, B, C, D, AB, AC, AD, and A² are significant model terms. P-values greater than 0.05 indicate that the model terms are not significant. However, the effect of pressure on the results is more pronounced as its F-value is greater than that of other terms in this study. The significant terms in the models are slightly different for H₂S and CO₂. For the H₂S solubility model, the square of temperature is a significant term, while for the CO₂, the square of pressure is a significant term in the fitted model.

Fit statistics show that the R² value for the model is 0.9951 and the predicted R² is 0.9881, while the Adeq precision is equal to 57.707. The Adeq precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. In this study, a ratio of 57.707 indicates an adequate signal. This model can be used to navigate the design space. Therefore, for CO₂ solubility prediction, this model can be used. The lack of fit is also not significant, which is an indication of good model fit.

The normal plot of residuals for the fitted model to the experimental data is presented in Fig. 4. As can be seen, the model can predicts the experimental data considering the value of R-square.

For H₂S, the ratio of minimum and maximum response value was 18950, which is four orders of magnitude difference; therefore, a transformation of the response values is required. In this study, the root square function in the form of $y' = \sqrt{y + 0.5}$ was used for data transformation. The ANOVA results for H₂S response is shown in Table 4.

Fit statistics show that the R² value for the model is 0.9914 and the predicted R² is 0.9793, while Adeq precision is equal to 46.01. In this study, a ratio of 46.01 indicates an adequate signal. This model can be used to navigate the design space. Therefore, this model can be used for the H₂S solubility prediction.

The model F-value of 230.72 implies that the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate that the model terms are significant. In this case, A, B, C, AB, and AC are significant model terms. P-values greater than 0.050 indicate that the model terms are not significant. The Lack of Fit F-value of 0.0628 implies that the Lack of Fit is insignificant relative to the pure error. There is a 6.28% chance that a Lack of Fit F-value this large could occur due to noise. Not-significant lack of fit is good and shows that the model is fitted properly to the experimental data. The normal plot of residue shown in Fig. 5.

The final equation for the model for both H₂S and CO₂ solubility in the mixture of amine+ ILs solvent, is presented in Table 5.

As can be seen from the Table 5, the pressure, temperature and ionic liquid loading in the solvent have a significant effects and contribute to most of solubility on acid gases in the solvent. However, based on Table 5, the [Bmim][Ac] yield better results in term of CO₂ and H₂S solubility.

In order to find the optimum condition for the highest solubility of H₂S and CO₂ from fitted models, the optimization of the model is conducted in the design expert software, and the results indicate that the optimum condition for the ILs that used in this study is as follows: The optimum pressure is 44 bar, the optimum temperature of absorption is 25 °C, the ILs percentage loading for [Bmim][Ac] is 10 (wt.%). In this optimum condition, the solubility of H₂S and CO₂ is 0.262 and 0.019, respectively, and desirability of these conditions is equal to unity.

Table 2: The Experimental Design Matrix

Run	Factor 1	Factor 2	Factor 3	Factor 4	Response 1	Response 2
	A:P	B:T	C:C	D:IL type	CO ₂ solubility	H ₂ S solubility
	[Bar]	[°C]	[%]	-	Mol frac.	Mol frac.
1	44	45	10	[Bmim][Ac]	0.24488	0.01486
2	44	65	10	[Hmim][NO ₃]	0.18598	0.013
3	21	65	20	[Hmim][NO ₃]	0.0281	0.00214
4	2	65	10	[Hmim][NO ₃]	5.29E-05	2.00E-05
5	2	25	10	[Bmim][Ac]	0.00419	1.00E-05
6	21	65	10	[Bmim][Ac]	0.05967	0.00455
7	30.5	45	15	[Bmim][Ac]	0.13278	0.00963
8	2	45	10	[Hmim][NO ₃]	0.00186	3.00E-05
9	44	65	10	[Hmim][NO ₃]	0.16548	0.01491
10	2	65	20	[Hmim][NO ₃]	3.21E-05	1.00E-06
11	44	65	20	[Hmim][NO ₃]	0.12087	0.00619
12	2	65	10	[Bmim][Ac]	5.25E-05	2.00E-05
13	44	25	15	[Hmim][NO ₃]	0.22156	0.0136
14	2	25	15	[Bmim][Ac]	0.00307	1.46E-05
15	2	45	20	[Bmim][Ac]	0.00164	1.00E-05
16	44	65	20	[Bmim][Ac]	0.14513	0.0087
17	2	65	20	[Bmim][Ac]	1.98E-05	1.00E-06
18	11.5	45	10	[Bmim][Ac]	0.0245	0.00241
19	21	25	20	[Bmim][Ac]	0.08142	0.0079
20	44	65	15	[Bmim][Ac]	0.18823	0.0124
21	11.5	45	20	[Hmim][NO ₃]	0.0145	0.00101
22	2	65	10	[Bmim][Ac]	5.25E-05	2.00E-05
23	2	25	20	[Hmim][NO ₃]	0.00269	1.00E-05
24	44	25	10	[Bmim][Ac]	0.25411	0.01889
25	11.5	65	15	[Bmim][Ac]	0.0155	0.00074
26	30.5	45	10	[Hmim][NO ₃]	0.12929	0.00958
27	2	25	20	[Hmim][NO ₃]	0.00271	1.00E-05
28	44	25	10	[Bmim][Ac]	0.25405	0.01895
29	21	25	10	[Hmim][NO ₃]	0.09412	0.00823
30	2	65	20	[Bmim][Ac]	2.09E-05	1.00E-06
31	2	25	10	[Hmim][NO ₃]	0.00408	7.00E-05
32	44	25	20	[Bmim][Ac]	0.21055	0.0134
33	44	65	20	[Bmim][Ac]	0.14419	0.0087
34	21	45	15	[Hmim][NO ₃]	0.05693	0.0047
35	44	25	20	[Bmim][Ac]	0.20073	0.0134
36	44	25	20	[Hmim][NO ₃]	0.16351	0.01021
37	44	45	20	[Hmim][NO ₃]	0.1386	0.00738
38	2	25	10	[Bmim][Ac]	0.00473	7.00E-05
39	44	25	10	[Hmim][NO ₃]	0.24696	0.01835
40	2	65	15	[Hmim][NO ₃]	4.48E-05	1.00E-06

Table 3: ANOVA for Quadratic Model for CO₂ Concentration Response

Source	Sum of	df	Mean	F-value	p-value
Model	0.3260	13	0.0251	404.46	< 0.0001
A-P	0.2729	1	0.2729	4400.53	< 0.0001
B-T	0.0082	1	0.0082	133.00	< 0.0001
C-C	0.0075	1	0.0075	121.27	< 0.0001
D-IL type	0.0017	1	0.0017	27.17	< 0.0001
AB	0.0043	1	0.0043	69.56	< 0.0001
AC	0.0063	1	0.0063	101.37	< 0.0001
AD	0.0015	1	0.0015	24.12	< 0.0001
BC	8.398E-06	1	8.398E-06	0.1354	0.7158
BD	9.986E-06	1	9.986E-06	0.1610	0.6915
CD	0.0002	1	0.0002	3.95	0.0575
A ² ₁	0.0028	1	0.0028	45.26	< 0.0001
B ² ₁	3.300E-07	1	3.300E-07	0.0053	0.9424
C ² ₁	0.0002	1	0.0002	2.52	0.1241
Residual	0.0016	26	0.0001		
Lack of Fit	0.0014	18	0.0001	2.32	0.1126
Pure Error	0.0003	8	0.0000		
Cor Total	0.3276	39			

Table 3: The ANOVA Results for H₂S Solubility Response

Source	Sum of	df	Mean	F-value	p-value
Model	0.0008	13	0.0001	230.72	< 0.0001
A-P	0.0006	1	0.0006	2344.88	< 0.0001
B-T	0.0000	1	0.0000	91.08	< 0.0001
C-C	0.0000	1	0.0000	139.98	< 0.0001
D-IL type	4.255E-06	1	4.255E-06	16.44	0.0004
AB	0.0000	1	0.0000	41.39	< 0.0001
AC	0.0000	1	0.0000	135.52	< 0.0001
AD	2.913E-06	1	2.913E-06	11.26	0.0024
BC	1.609E-07	1	1.609E-07	0.6216	0.4376
BD	6.850E-07	1	6.850E-07	2.65	0.1158
CD	4.333E-06	1	4.333E-06	16.74	0.0004
A ² ₁	1.265E-07	1	1.265E-07	0.4888	0.4907
B ² ₁	1.519E-06	1	1.519E-06	5.87	0.0227
C ² ₁	9.278E-09	1	9.278E-09	0.0358	0.8513
Residual	6.729E-06	26	2.588E-07		
Lack of Fit	5.840E-06	18	3.245E-07	2.92	0.0628
Pure Error	8.890E-07	8	1.111E-07		
Cor Total	0.0008	39			

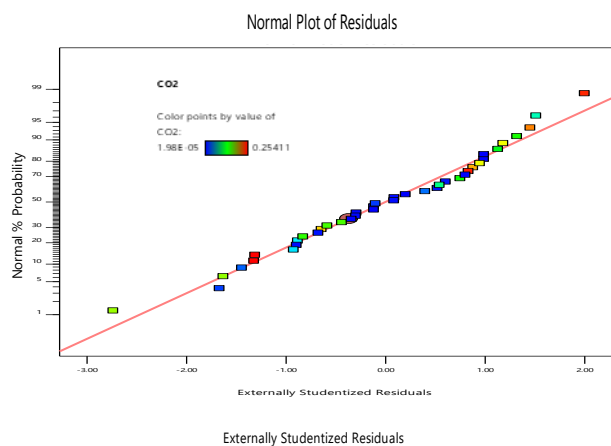


Fig. 3: Residual Plot of The Fitted Model to the Design Matrix Data for CO₂

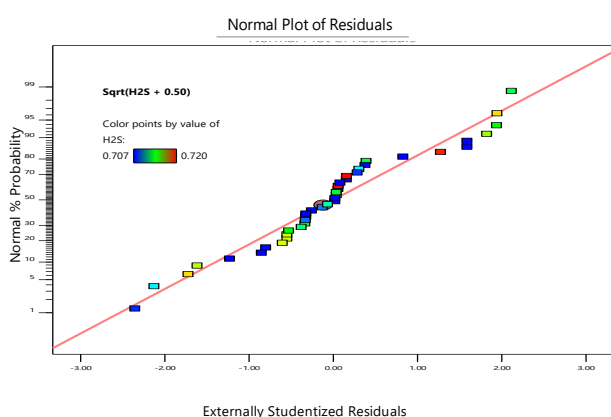


Fig. 4: Residual Plot of Fitted Model to the Design Matrix Data

Based on the results obtained in this work, considering a large-scale sweet gas processing plant that operates with MDEA amine at pressure and temperature range tested in this work, it can be concluded that a hybrid solvent of 30% MDEA and 10% [Bmim][Ac] has higher performance than amine solvent alone for removal of CO₂ and H₂S from a real natural gas. However, it must be noted that based on the H₂S solubility results, lower H₂S loading can be expected from such a hybrid solvent. It is safe to say that a hybrid solvent of 10% [Bmim][Ac] and 30% MDEA is more suitable for natural gas feeds that have lower H₂S and higher CO₂ impurities.

CONCLUSION

In this work, the solubility of a real sour natural gas mixture was investigated in conventional amine solvent and hybrid solvents of amine with two different ionic liquids solvents at different percentages of ILs. The pressure and temperature range were selected based on a large-scale acid gas sweetening process. The loading percentage of ILs

changed from 10 to 20% in the MDEA amine. The results indicate that the addition of 10% ILs to the amine solvent can increase the solubility of CO₂ but reduce the solubility of H₂S. The higher ILs loading to the amine solvent have a diverse effect on the solubility of acid gas and hydrocarbons. Increasing pressure increased the solubility of the acid gases in both MDEA and hybrid solvents. In addition, increasing the temperature caused a reduction in solubility of acid gas in the solvents. However, the effect of temperature on solubility reduction is more pronounced for the hybrid solvents in comparison to the MDEA alone. The effect of temperature on the H₂S solubility is more pronounced on the [Bmim][Ac] solvent compared to [Hmim][NO₃]. This finding indicates that formulating of a proper amine and IL solvent has an optimum value for amine and ILs in the mixture solvent. An experimental design approach was employed to obtain a proper formulation for synthesizing the optimum hybrid solvent. The results imply that the pressure, temperature and ILs loading in the hybrid solvent have a pronounced effect on the solubility of real natural gas mixture, and [Bmim][Ac] ionic liquid is better solvent for synthesizing a hybrid solvent for acid gas sweetening process. Also, it was concluded that hybrid solvent that introduced in this study, has more affinity toward CO₂ absorption, therefore, it is more suitable for natural gases with higher CO₂ and lower H₂S concentrations. However, more work is required to investigate this matter before use it in an industrial-scale application.

Abbreviations

ANOVA	Analysis of variance
A	Coded variable in experimental design represent Pressure
B	Coded variable in experimental design represent Temperature
C	Coded variable in experimental design represent Concentration
D	Coded variable in experimental design represent type of ionic liquid
DEA	Diethanolamine
DIPA	Di-iso-propanolamine
IL	Ionic liquid
MEA	Monoethanolamine
P	Pressure [bar]
T	Temperature [K]
x	Solubility []

Table 5: Final Model for H₂S and CO₂ Concentration Prediction

Sqrt(H ₂ S + 0.50)	=	CO ₂	=
IL type	[Bmim][Ac]	IL type	[Bmim][Ac]
+0.707636		-0.053986	
+0.000448	P	+0.006047	P
-0.000117	T	-0.000123	T
+0.000103	C	+0.007024	C
-1.54276E-06	P * T	-0.000031	P * T
-0.000011	P * C	-0.000149	P * C
-7.97276E-07	T * C	+5.76011E-06	T * C
+3.56474E-07	P ²	+0.000053	P ²
+1.24664E-06	T ²	-5.81093E-07	T ²
+1.63660E-06	C ²	-0.000213	C ²
IL type	[Hmim][NO ₃]	IL type	[Hmim][NO ₃]
+0.709177		-0.032611	
+0.000418	P	+0.005377	P
-0.000102	T	-0.000181	T
-0.000044	C	+0.005918	C
-1.54276E-06	P * T	-0.000031	P * T
-0.000011	P * C	-0.000149	P * C
-7.97276E-07	T * C	+5.76011E-06	T * C
+3.56474E-07	P ²	+0.000053	P ²
+1.24664E-06	T ²	-5.81093E-07	T ²
+1.63660E-06	C ²	-0.000213	C ²

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REFERENCES

- [1] Jamali S.H., Ramdin M., Becker T.M., Torres-Knoop A., Dubbeldam D., Buijs W., Vlught T.J.H., Solubility of Sulfur Compounds in Commercial Physical Solvents and an Ionic Liquid from Monte Carlo Simulations, *Fluid Phase Equilib.*, **433**: 50–55 (2017).
- [2] Álvarez-Gutiérrez N., Gil M. V., Rubiera F., Pevida C., Kinetics of CO₂ Adsorption on Cherry Stone-Based Carbons in CO₂/CH₄ Separations, *Chem. Eng. J.*, **307**: 249–257 (2017).
- [3] Tagliabue M., Farrusseng D., Valencia S., Aguado S., Ravon U., Rizzo C., Corma A., Mirodatos C., Natural Gas Treating by Selective Adsorption: Material Science and Chemical Engineering Interplay, *Chem. Eng. J.*, **155**: 553–566 (2009).
- [4] Scholes C.A., Stevens G.W., Kentish S.E., Membrane Gas Separation Applications in Natural Gas Processing, *Fuel*, **96**: 15–28 (2012).
- [5] Kailasa S.K., Koduru J.R., Vikrant K., Tsang Y.F., Singhal R.K., Hussain C.M., Kim K.-H.H., Recent Progress on Solution and Materials Chemistry for the Removal of Hydrogen Sulfide from Various Gas Plants, *J. Mol. Liq.*, **297**: 111886 (2020).
- [6] Ashrafmansouri S.-S., Vapor-Liquid Equilibrium of Binary Systems Containing Cyano-Based Ionic Liquids and CO₂: SAFT- γ GC EoS Modeling, *Iran. J. Chem. Chem. Eng.*, **41**: 12,4144–4151 (2022)
- [7] Rufford T.E., Smart S., Watson G.C.Y., Graham B.F., Boxall J., Diniz da Costa J.C., May E.F., The removal of CO₂ and N₂ from Natural gas: A Review of Conventional and Emerging Process Technologies, *J. Pet. Sci. Eng.*, **94–95**: 123–154 (2012).
- [8] Jamekhorshid A., Karimi Davani Z., Salehi A., Khosravi A., Gas Sweetening Simulation and its Optimization by two Typical Amine Solutions: An Industrial Case Study in Persian Gulf region, *Nat. Gas Ind. B.*, **8**: 309–316 (2021).

- [9] Aronu U.E., Svendsen H.F., Hoff K.A., Juliussen O., [Solvent Selection for Carbon Dioxide Absorption](#), *Energy Procedia.*, **1**: 1051–1057(2009)
- [10] Qayyum A., Ali U., Ramzan N., [Acid Gas Removal Techniques for Syngas, Natural Gas, and biogas clean Up—A Review](#), *Energy Sources, Part A Recover. Util. Environ. Eff.*, **00**: 1–24 (2020).
- [11] Shojaeian A., Haghtalab A., [Solubility and Density of Carbon Dioxide in Different Aqueous Alkanolamine Solutions Blended with 1-Butyl-3-Methylimidazolium Acetate Ionic Liquid at High Pressure](#), *J. Mol. Liq.*, **187**: 218–225 (2013).
- [12] Tanthana J., Rayer A.V., Gupta V., Mobley P.D., Soukri M., Zhou J., Lail M., [Experimental Study of a Hydrophobic Solvent for Natural Gas Sweetening Based on the Solubility and Selectivity for Light Hydrocarbons \(CH₄, C₂H₆\) and Acid Gases \(CO₂ and H₂S\) at 298–353 K](#), *J. Chem. Eng. Data*, **64**: 545–556 (2019).
- [13] Lawson J.D., Garst A.W., [Gas Sweetening Data: Equilibrium Solubility of Hydrogen Sulfide and Carbon Dioxide in Aqueous Monoethanolamine and Aqueous Diethanolamine Solutions](#), *J. Chem. Eng. Data*, **21**: 20–30 (1976).
- [14] Rochelle G.T., [Amine Scrubbing for CO₂ Capture](#), *Science*, **325**: 1652–1654 (2009).
- [15] Lu J.G., Zheng Y.F., He D.L., [Selective Absorption of H₂S from Gas Mixtures into Aqueous Solutions of Blended Amines of Methyl-diethanolamine and 2-Tertiarybutylamino-2-Ethoxyethanol in a Packed Column](#), *Sep. Purif. Technol.*, **52**: 209–217 (2006).
- [16] Penttilä A., Dell’Era C., Uusi-Kyyny P., Alopaeus V., [The Henry’s Law Constant of N₂O and CO₂ in Aqueous Binary and Ternary Amine Solutions \(MEA, DEA, DIPA, MDEA, and AMP\)](#), *Fluid Phase Equilib.*, **311**: 59–66 (2011).
- [17] Fouad W.A., Berrouk A.S., [Using Mixed Tertiary Amines for Gas Sweetening Energy Requirement Reduction](#), *J. Nat. Gas Sci. Eng.*, **11**: 12–17 (2013).
- [18] Feng Z., Jing-Wen M., Zheng Z., You-Ting W., Zhi-Bing Z., [Study on the Absorption of Carbon Dioxide in High Concentrated MDEA and ILs Solutions](#), *Chem. Eng. J.*, **181–182**: 222–228 (2012).
- [19] Mortazavi-Manesh S., Satyro M.A., Marriott R.A., [Screening Ionic Liquids as Candidates for Separation of Acid Gases: Solubility of Hydrogen Sulfide, Methane, and Ethane](#), *AIChE J.*, **59**: 2993–3005 (2013).
- [20] Althuluth M., Overbeek J.P., van Wees H.J., Zubeir L.F., Haije W.G., Berrouk A., Peters C.J., Kroon M.C., [Natural Gas Purification using Supported Ionic Liquid Membrane](#), *J. Memb. Sci.*, **484**: 80–86 (2015).
- [21] Camper D., Bara J.E., Gin D.L., Noble R.D., [Room-Temperature Ionic Liquid–Amine Solutions: Tunable Solvents for Efficient and Reversible Capture of CO₂](#), *Ind. Eng. Chem. Res.*, **47**: 8496–8498 (2008).
- [22] Kumar S., Cho J.H., Moon I., [Ionic Liquid-Amine Blends and CO₂BOLs: Prospective Solvents for Natural Gas Sweetening and CO₂ Capture Technology-A Review](#), *Int. J. Greenh. Gas Control.*, **20**: 87–116 (2014).
- [23] Feng Z., Cheng-Gang F., You-Ting W., Yuan-Tao W., Ai-Min L., Zhi-Bing Z., [Absorption of CO₂ in the Aqueous Solutions of Functionalized Ionic Liquids and MDEA](#), *Chem. Eng. J.*, **160**: 691–697 (2010).
- [24] Taib M.M., Murugesan T., [Solubilities of CO₂ in Aqueous Solutions of Ionic Liquids \(ILs\) and Monoethanolamine \(MEA\) at Pressures from 100 to 1600kPa](#), *Chem. Eng. J.*, **181–182**: 56–62 (2012).
- [25] Ahmady A., Hashim M.A., Aroua M.K., [Absorption of Carbon Dioxide in the Aqueous Mixtures of Methyl-diethanolamine with three Types of Imidazolium-Based Ionic Liquids](#), *Fluid Phase Equilib.*, **309**: 76–82 (2011).
- [26] Shin E.K., Lee B.C., [High-Pressure Phase Behavior of Carbon Dioxide with Ionic Liquids: 1-alkyl-3-Methylimidazolium Trifluoromethanesulfonate](#), *J. Chem. Eng. Data*, **53**: 2728–2734 (2008).
- [27] Haghtalab A., Shojaeian A., [High Pressure Measurement and Thermodynamic Modelling of the Solubility of Carbon Dioxide in N-Methyl-diethanolamine and 1-Butyl-3-Methylimidazolium Acetate Mixture](#), *J. Chem. Thermodyn.*, **81**: 237–244 (2015).
- [28] Cadena C., Anthony J.L., Shah J.K., Morrow T.I., Brennecke J.F., Maginn E.J., [Why Is CO₂ So Soluble in Imidazolium-Based Ionic Liquids?](#), *J. Am. Chem. Soc.*, **126**: 5300–5308 (2004).
- [29] Safarov J., Geppert-Rybczyńska M., Kul I., Hassel E., [Thermophysical Properties of 1-Butyl-3-Methylimidazolium Acetate Over a Wide Range of Temperatures and Pressures](#), *Fluid Phase Equilib.*, **383**: 144–155 (2014).
- [30] Khedri Z., Almasi M., Maleki A., [Thermodynamic Properties of 1-Hexyl-3-Methylimidazolium Nitrate and 1-Alkanols Mixtures: PC-SAFT Model](#), *J. Chem. Eng. Data*, **64**: 4465–4473 (2019).

- [31] Shaahmadi F., Hashemi Shahraki B., Farhadi A., [The CO₂/CH₄ Gas Mixture Solubility in Ionic Liquids \[Bmim\]\[Ac\], \[Bmim\]\[BF₄\] and their Binary Mixtures](#), *J. Chem. Thermodyn.*, **141**: 105922 (2020).
- [32] Rezaeinejad R., Sharif A.A.M., Shaahmadi F., [Separation of CO₂ and H₂S from Natural Gas of Iranian Gas Refinery Using Ionic Liquids: Experimental Measurements and Thermodynamic Modeling](#), *Korean J. Chem. Eng.*, **40**: 925-934 (2023).
- [33] Hailegiorgis S.M., Khan S.N., Abdolah N.H.H., Ayoub M., Tesfamichael A., [Carbon Dioxide Capture via Aqueous N-Methyldiethanolamine \(MDEA\)-1-butyl-3-Methylimidazolium Acetate \(\[bmim\]\[Ac\]\) Hybrid Solvent](#), *AIP Conf. Proc.*, 1891 (2017).
- [34] Ramdin M., Balaji S.P., Torres-Knoop A., Dubbeldam D., de Loos T.W., Vlught T.J.H., [Solubility of Natural Gas Species in Ionic Liquids and Commercial Solvents: Experiments and Monte Carlo Simulations](#), *J. Chem. Eng. Data*, **60**: 3039–3045 (2015).
- [35] Shaahmadi F., Hashemi Shahraki B., Farhadi A., [The Solubility of Carbon Dioxide and Density for Binary Mixtures of 1-Butyl-3-Methylimidazolium Acetate and 1-Butyl-3-Methylimidazolium Tetrafluoroborate](#), *J. Chem. Eng. Data*, **64**: 584–593 (2019).
- [36] Cabac M.I., Besnard M., Danten Y., Coutinho J.A.P., [Carbon Dioxide in 1-Butyl-3-Methylimidazolium Acetate . I . Unusual Solubility Investigated by Raman Spectroscopy and DFT Calculations](#), *J. Phys. Chem. A.*, **116**: 1605–1620 (2012).
- [37] Cui G., Wang J., Zhang S., [Active Chemisorption Sites in Functionalized Ionic Liquids for Carbon Capture](#), *Chem. Soc. Rev.*, **45**: 4307–4339 (2016).
- [38] Cao L., Gao J., Zeng S., Dong H., Gao H., Zhang X., Huang J., [Feasible Ionic Liquid-Amine Hybrid Solvents for Carbon Dioxide Capture](#), *Int. J. Greenh. Gas Control.*, **66**: 120–128 (2017).