

## Article

# Research and Performance Evaluation on Selective Absorption of H<sub>2</sub>S from Gas Mixtures by Using Secondary Alkanolamines

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**Abstract:** Exploring new solvents for efficient acid gas removal is one of the most attractive topics in industrial gas purification. Herein, using 2-tertiarybutylamino-2-ethoxyethanol as an absorbent in a packed column at atmospheric pressure was examined for selective absorption of H<sub>2</sub>S from mixed gas streams. In the present work, the acid gas load, H<sub>2</sub>S absorption selectivity, acid gas removal ratio, amine solution regeneration performance, and corrosion performance were investigated through evaluating experiments absorbing H<sub>2</sub>S and CO<sub>2</sub> by using methyldiethanolamine and 2-tertiarybutylamino-2-ethoxyethanol. The experimental results illustrate that the H<sub>2</sub>S absorption selective factors were 3.88 and 15.81 by using 40% methyldiethanolamine and 40% 2-tertiarybutylamino-2-ethoxyethanol at 40 °C, respectively, showing that 2-tertiarybutylamino-2-ethoxyethanol is an efficient solvent for selective H<sub>2</sub>S removal, even better than methyldiethanolamine. Based on the consideration of cost, we added 5% TBEE to 35% MDEA to form a blended aqueous solvent. To our satisfaction, the blended amine solvent obtained a 99.79% H<sub>2</sub>S removal rate and a 22.68% CO<sub>2</sub> co-absorption rate, while using the methyldiethanolamine alone achieved a 98.33% H<sub>2</sub>S removal rate and a 23.52% CO<sub>2</sub> co-absorption rate; the blended solvent showed better H<sub>2</sub>S absorption efficiency and selectivity. Taken together, this work provides valuable information for a promising alkanolamine for acid gas removal, and the preliminary study has found that the aqueous blend of methyldiethanolamine and 2-tertiarybutylamino-2-ethoxyethanol is an efficient solvent for selective H<sub>2</sub>S removal, which not only extends the application field for sterically hindered amines, but also opens up new opportunities in blended solvent design.

**Keywords:** selective H<sub>2</sub>S removal; acid gas absorption; alkanolamine solution; gas mixture separation; 2-tertiarybutylamino-2-ethoxyethanol



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## 1. Introduction

In the industrial gas purification process, removal of acid gas impurities such as H<sub>2</sub>S and CO<sub>2</sub> is a significant technical issue which has drawn considerable attention from scientists around the world. The existence of acid impurities in the gas mixtures could cause a series of severe problems, such as catalyst poisoning, equipment corrosion, and environmental pollution. Therefore, the acid gas impurities should be well removed to meet the requirements of emission standards. Generally, the principal technologies for acid gas impurity removal include absorption and adsorption. Over recent years, the study of CO<sub>2</sub> and H<sub>2</sub>S absorption abilities of different solvents has been introduced [1,2]. Moreover, the solubility of a CO<sub>2</sub> and H<sub>2</sub>S gas mixture in aqueous methyldiethanolamine (MDEA) [3,4] and the simultaneous removal of multiple acid gases in sulfolane–MDEA solvent were reported [5]. Up to now, in addition to the alkanolamine absorption, several technologies have been developed for CO<sub>2</sub> and H<sub>2</sub>S removal, including modified activated carbons [6], membrane technology [7,8], ionic liquids, and deep eutectic solvents [9,10].

Currently, the chemical absorption of acid gas by aqueous solutions of alkanolamines is the most attractive purification method in the industry.

Commonly, commercially available alkanolamines, including but not limited to monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), and MDEA, were employed in the chemical absorption approach. Among them, MDEA is the most widely used absorption solvent for acid gas removal due to its performance advantages in H<sub>2</sub>S selectivity, absorption capacity, regeneration energy, and corrosion resistance [11]. However, in order to promote the absorption performance of the MDEA solvent, several blended solvents created by adding other components into an MDEA solution have been developed since the 1980s, including MDEA–MEA [12], MDEA–piperazine [13] and MDEA–DGA (DGA: 2-(2-aminoethoxy)ethanol) [14]. Usually, blended solvents can exhibit the advantages of each component [15], thus not only resulting in a higher reaction rate, but also reducing regeneration energy depletion.

Although blended solvents have been developed and used widely, several urgent issues still remain to be addressed in industrial applications, such as highly selective H<sub>2</sub>S removal. To address this problem, the Exxon Research and Engineering Company has developed several sterically hindered amines such as 2-isopropylaminoethanol (IPAE), 2-tertiarybutylaminoethanol (TBE), 2-tertiarybutylamino-2-ethoxyethanol (TBEE), and N-tertiary butyl glycine (TBG). Sterically hindered amines are an amine compound with a bulky alkyl group attached to the N atom in the amine group. It should be noted that because of the steric hindrance effect of the bulky alkyl group on the amine group, the amine group is more active [16,17]. Therefore, the sterically hindered amine may be a potentially attractive solvent for acid gas removal. Inspired by the pioneering work on sterically hindered amines employed in gas sweetening processes [17], a series of significant investigations have also been reported in the past decades. Weiland [18] and Li [19] studied the solubilities of CO<sub>2</sub> and H<sub>2</sub>S in hindered amines containing aqueous alkanolamine solutions. Saha [20] and Mandal [21] revealed that 2-amino-2-methyl-1-propanol (AMP) has better selectivity for H<sub>2</sub>S removal in the presence of CO<sub>2</sub> in acid gas streams. In 2005, Mandal et al. [22] reported an experimental and theoretical investigation of absorption of CO<sub>2</sub> and H<sub>2</sub>S using an aqueous blended solution of AMP and DEA. Subsequently, a blended solution consisting of MDEA and TBEE for highly selective H<sub>2</sub>S removal from mixed gas streams containing CO<sub>2</sub> and H<sub>2</sub>S was reported by Zheng et al. in 2006 [23]. However, to the best of our knowledge, the study of TBEE performance evaluation is still rare; further investigation is needed to elucidate its absorption ability and direct the formulation of efficient mixed solvents.

In the present work, the acid gas load, H<sub>2</sub>S absorption selectivity, acid gas removal ratio, amine solution regeneration performance, and corrosion performance of the sterically hindered amine TBEE in a packed column at atmospheric pressure were investigated. Furthermore, the performance of a blended aqueous solvent that consisted of 5% TBEE and 35% MDEA was examined. This work indicates that TBEE is a promising alkanolamine for selective H<sub>2</sub>S removal, with broad application prospects in the gas purification field.

## 2. Theoretical Basis

### 2.1. Characteristics of Molecular Structure

Amines can be classified into primary, secondary, and tertiary amines based on the number of protons attached to the N atom. TBEE and MDEA are secondary and tertiary amines, respectively. However, from the perspective of amine molecular structure, TBEE belongs to sterically hindered amines, and sterically hindered amines refer to amines with several substituent groups on the  $\alpha$ -carbon atom connected to the amino group in the molecular structure, thus having a significant steric hindrance effect. The steric hindrance of the alkyl group makes the amino group of TBEE have a higher chemical activity than the non-sterically hindered amine. The steric hindrance effect of different substituent groups (defined as R or R' in Table 1) can be represented by the steric hindrance constant  $E_s$ . D.

F. Detar [24] obtained the Taft steric hindrance coefficient  $E_s$  of several alkyl groups by studying the ester hydrolysis reaction of the  $S_N2$  reaction mechanism, as shown in Table 1.

**Table 1.** Taft alkyl steric hindrance constants.

R	$E_s$ Value	R'	$E_s$ Value
-CH <sub>3</sub>	0.07	-CH <sub>2</sub> CH <sub>2</sub> OH	0.36
-CH <sub>2</sub> CH <sub>3</sub>	0.36	-(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> H	0.36
-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	0.39	-CH(CH <sub>3</sub> )CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	0.93
-CH(CH <sub>3</sub> ) <sub>2</sub>	0.93	-C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	1.74
-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	0.41	-C(CH <sub>3</sub> )(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub>	1.74
-CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	0.43	-C(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>3</sub>	1.74
-CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub>	0.96		
-C(CH <sub>3</sub> ) <sub>3</sub>	1.74		

The acidity and alkalinity of the molecule is characterized by pKa, which refers to the acidity coefficient, also known as the acid dissociation constant, which in chemistry refers to a specific equilibrium constant that represents the ability of an acid to dissociate hydrogen ions. For amine molecules, it essentially implies the binding ability of the lone pair of electrons and protons on the N atom in the molecule. Due to the existence of its adjacent substituent groups, its ability to bind with protons is weakened to different degrees, resulting in different pKas of different amines. The stronger the basicity of the amine, the larger the pKa value, and the faster the reaction rate with acid gas; that is, the value of the pKa of an amine represents the reactivity of the amine with acid gases. Generally, the pKa value of sterically hindered amines is 9.5–10.6 [21].

## 2.2. Reaction Mechanism

Generally, absorption of H<sub>2</sub>S/CO<sub>2</sub> into secondary or tertiary amines is through different reaction mechanisms. The reaction of CO<sub>2</sub> with different alkanolamines has been widely reported, including MEA, DEA [25], DIPA [26], and AMP [27,28]. Accordingly, it is generally accepted that CO<sub>2</sub> reacts with secondary amines through a zwitterionic mechanism as follows:



In Equation (2), B is a basic amine, OH<sup>-</sup> or H<sub>2</sub>O [25]. Subsequently, the hydrolytic reaction occurs as Equation (3) [27]:



Accordingly, the overall reaction can be presented as:

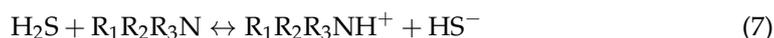


Obviously, the abovementioned reaction mechanism implies that the final product of the CO<sub>2</sub>-R<sub>1</sub>R<sub>2</sub>NH reaction is bicarbonate. Similarly, CO<sub>2</sub> can react with MDEA in the presence of water to generate bicarbonate, and the overall reaction is as follows:



In addition, the reaction mechanism between H<sub>2</sub>S and secondary and tertiary amines can be described as Equations (6) and (7):





According to the literature's reported data, the reaction rate constant  $k$  values of Equations (4) and (5) are about  $3.7\text{--}7.5 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$  [29], whereas the reaction rate constant  $k$  values of Equations (6) and (7) are up to  $10^9 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$  [30]. From the perspective of kinetics, the reactions between  $\text{CO}_2$  and  $\text{H}_2\text{S}$  with secondary amines (hindered amines) and tertiary amines are distinct. Accordingly, the hindered amine may have a higher  $\text{H}_2\text{S}$  selectivity capacity.

### 2.3. Absorption Performance Evaluation Calculation Method

#### (1) Acid gas load

The acid gas load of the solution is the sum of the  $\text{H}_2\text{S}$  load ( $L_{\text{H}_2\text{S}}$ ) and the  $\text{CO}_2$  load ( $L_{\text{CO}_2}$ ) in the liquid. It can be calculated by the following equations:

$$L_{\text{H}_2\text{S}} = \frac{\text{Molar amount of H}_2\text{S in liquid phase}}{\text{Molar amount of amine in liquid phase}} \quad (8)$$

$$L_{\text{CO}_2} = \frac{\text{Molar amount of CO}_2 \text{ in liquid phase}}{\text{Molar amount of amine in liquid phase}} \quad (9)$$

#### (2) Removal efficiency

The absorption performance of the desulfurizer can be measured by the desulfurization rate of  $\text{H}_2\text{S}$  ( $\eta_s$ ) and the removal rate of  $\text{CO}_2$  ( $\eta_c$ ). The higher the  $\eta_s$  is, the better the desulfurization performance of the desulfurizer is. In the selective desulfurization process,  $\text{CO}_2$  in the liquid phase will affect the absorption of  $\text{H}_2\text{S}$  by the desulfurizing solution, so the lower the  $\eta_c$  is, the better the performance of  $\text{H}_2\text{S}$  absorption is. The value of  $\eta_s$  and  $\eta_c$  can be calculated by the following Equations (10) and (11) based on the material balance:

$$\eta_s = 1 - \frac{y'_{\text{H}_2\text{S}}}{y_{\text{H}_2\text{S}}} \cdot \frac{1 - y_{\text{H}_2\text{S}} - y_{\text{CO}_2}}{1 - y'_{\text{H}_2\text{S}} - y'_{\text{CO}_2}} \quad (10)$$

$$\eta_c = 1 - \frac{y'_{\text{CO}_2}}{y_{\text{CO}_2}} \cdot \frac{1 - y_{\text{H}_2\text{S}} - y_{\text{CO}_2}}{1 - y'_{\text{H}_2\text{S}} - y'_{\text{CO}_2}} \quad (11)$$

$y_{\text{H}_2\text{S}}$ —molar fraction of  $\text{H}_2\text{S}$  in feed gas;  $y_{\text{CO}_2}$ —molar fraction of  $\text{CO}_2$  in feed gas;  
 $y'_{\text{H}_2\text{S}}$ —the mole fraction of  $\text{H}_2\text{S}$  in the tail gas;  $y'_{\text{CO}_2}$ —the mole fraction of  $\text{CO}_2$  in the tail gas.

#### (3) Selectivity factor

The selectivity of the desulfurization solvent can be expressed by the selectivity factor  $S$ .  $S$  is defined as the ratio of the molar ratio of removed  $\text{H}_2\text{S}$  to  $\text{CO}_2$  to the molar ratio of  $\text{H}_2\text{S}$  to  $\text{CO}_2$  in the feed gas. The calculation formula for selectivity  $S$  is as follows:

$$S = \frac{x_{\text{H}_2\text{S}}/x_{\text{CO}_2}}{y_{\text{H}_2\text{S}}/y_{\text{CO}_2}} \quad (12)$$

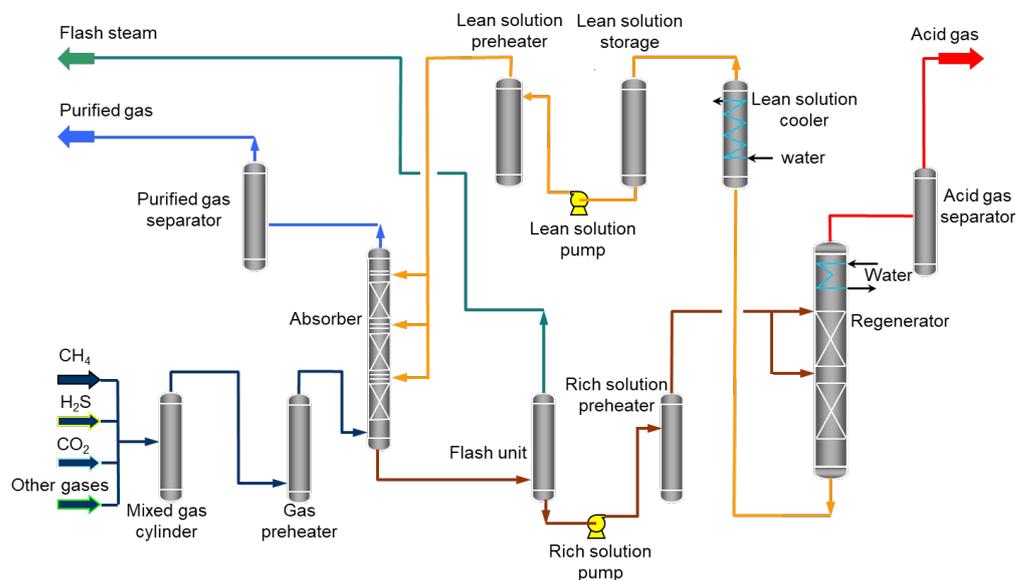
$x_{\text{H}_2\text{S}}$ —the amount of  $\text{H}_2\text{S}$  in the liquid phase, mol;  $x_{\text{CO}_2}$ —the amount of  $\text{CO}_2$  in the liquid phase, mol.

## 3. Experimental Section

### 3.1. Experimental Apparatus and General Procedure

The apparatus used in this project was the atmospheric pressure amine method desulfurization test device, as shown in Figure 1. Both the absorption tower and the regeneration tower of the apparatus are packed towers, and the absorption tower is provided with a lean liquid inlet at the packing heights of 0.5 m, 1.0 m, and 1.5 m.  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ ,  $\text{CO}_2$  and other gases enter the absorption tower after mixing in the mixed gas cylinder; the purified gas from the top of the absorption tower is separated by a separator and then measured

by a gas meter; the rich liquid from the bottom of the absorption tower is preheated by a pre-heater, then it enters the regeneration tower for regeneration, and the regenerated lean liquid is pumped into the absorption tower for recycling.



**Figure 1.** Schematic diagram of experimental apparatus for absorption of acid gases.

In order to further clarify how many trays in an industrial absorption tower are equivalent to the absorption effect of the laboratory atmospheric packed tower device at a packing height of 1.0 m, a comparative experiment was carried out using the data of the sulfur recovery hydrotreating tail gas desulfurization industrial unit in this work. As shown in Table S1, the absorption results of the atmospheric pressure amine desulfurization test device at a packing height of 1.0 m are close to the absorption results under 10 trays of the industrial apparatus. It can be considered that the 1.0 m packing of the atmospheric pressure amine desulfurization test device is roughly equivalent to 10 actual trays. It is more appropriate to use 10 to 12 plates for the hydrogenation tail gas absorption column in the industrial device. Therefore, the absorption performance data of the solution in this study were obtained at a packing height of 1.0 m (i.e., about 10 absorption trays) unless otherwise specified.

### 3.2. Materials and Analytical Methods

In this work,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , and MDEA were all purchased commercially; the purities of all gases were more than 99.99% and the purity of the MDEA was 99.5%. Moreover, TBEE was synthesized in the laboratory and the  $^1\text{H}$  NMR spectrum is present in the supporting information. The analytical method for determining the total amine concentration was using a methyl orange indicator by titration with a standard  $0.1 \text{ kmol/m}^3 \text{ H}_2\text{SO}_4$  solution. In addition, the contents of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  in the mixed gases were analyzed by gas chromatography.  $\text{H}_2\text{S}$  content in the liquid phase was determined by titration with standard  $0.1 \text{ kmol/m}^3 \text{ AgNO}_3$  solution. The analytical method for determining the  $\text{CO}_2$  content in the liquid phase was to use a known volume of the liquid sample after diluting it with a 1:4 aqueous  $\text{H}_2\text{SO}_4$  solution and measuring the volume of the evolved gas with a gas burette.

## 4. Results and Discussion

Initially, according to the experimental apparatus, experimental procedure, and reaction conditions described in the experimental section, the atmospheric desulfurization performance evaluation of the MDEA solution and the TBEE solution were carried out by simulating real working conditions. Detailed experimental results of  $\text{H}_2\text{S}$  and  $\text{CO}_2$

absorption by the MDEA and TBEE solutions at different temperatures and concentrations are summarized in Tables 2 and 3.

**Table 2.** Experimental results of acid gas absorption by MDEA solution at different temperatures and concentrations.

Temperature (°C)	MDEA Concentration (%)	$x_{\text{H}_2\text{S}}$ (g/mL)	$x_{\text{CO}_2}$ (g/mL)	$L_{\text{H}_2\text{S}}$	$L_{\text{CO}_2}$	S
30	10	0.02605	0.06515	0.03105	0.07765	4.00
30	20	0.0466	0.1162	0.02775	0.06925	4.01
30	30	0.0647	0.162	0.0257	0.06435	3.99
30	40	0.08115	0.20675	0.02415	0.0616	3.93
30	50	0.10215	0.26115	0.02435	0.06225	3.91
40	10	0.0239	0.06	0.0285	0.0715	3.98
40	20	0.04495	0.11465	0.0268	0.0683	3.92
40	30	0.0616	0.16075	0.02445	0.06385	3.83
40	40	0.07785	0.20065	0.0232	0.0598	3.88
40	50	0.09075	0.23945	0.02165	0.05705	3.79
50	10	0.02055	0.0517	0.0245	0.0616	3.97
50	20	0.03895	0.10115	0.0232	0.06025	3.85
50	30	0.05975	0.1548	0.02375	0.0615	3.86
50	40	0.0693	0.17715	0.02065	0.0528	3.91
50	50	0.08185	0.21345	0.0195	0.05085	3.83
60	10	0.0193	0.0497	0.023	0.05925	3.88
60	20	0.03165	0.0828	0.01885	0.04935	3.82
60	30	0.04515	0.11735	0.01795	0.0466	3.85
60	40	0.05975	0.15835	0.0178	0.04715	3.77
60	50	0.07025	0.1897	0.01675	0.0452	3.70

In Table 2,  $x_{\text{H}_2\text{S}}$  is the  $\text{H}_2\text{S}$  absorption ability of 1 mL of amine solution, that is, it represents the sulfur capacity of this amine solution at this concentration. Similarly,  $x_{\text{CO}_2}$  is the  $\text{CO}_2$  absorption ability of 1 mL of amine solution. The results in Table 2 exhibited that with the increase in amine concentration, both  $x_{\text{H}_2\text{S}}$  and  $x_{\text{CO}_2}$  tend to increase, but  $x_{\text{H}_2\text{S}}$  and  $x_{\text{CO}_2}$  do not exhibit a linear relationship with the amine concentration. The results imply that a lower concentration of amine liquid could benefit the mass transfer for liquid absorption. Notably, when the amine concentration in the solution was lower, the amine molecules in the solution that react with the acid gas are more dispersed, meanwhile, the gas–liquid contact time during the process of transferring the gas into the liquid is longer. Therefore, simply increasing the amine concentration does not contribute to overall absorption efficiency. With the increase in reaction temperature, both  $x_{\text{H}_2\text{S}}$  and  $x_{\text{CO}_2}$  decrease. The absorption of acid gas by the amine liquid is an exothermic reaction, and the temperature increase will induce the absorption reaction to reverse. From the perspective of physical absorption, heating will lead to an increase in the equilibrium partial pressure of acid gas on the surface of the solution, making the thermodynamic effect exceed the kinetic effect of heating on the acceleration of the  $\text{CO}_2$  dissolution rate, which is generally unfavorable for absorption. It can be seen from the results that a lower temperature will cause a larger load of  $\text{H}_2\text{S}$  and  $\text{CO}_2$ , that is, the total acid gas load is larger. Industrially, the temperature of the absorption tower is determined by the lean amine liquid temperature, which is generally 40 °C.

The experimental results also reveal that a higher amine concentration gives a smaller load of  $\text{H}_2\text{S}$  and  $\text{CO}_2$ , that is, a smaller total acid gas load. Theoretically, the concentration of the amine solution does not affect the size of the acid gas load, but in the actual absorption process, the amine concentration increase makes the amine molecules distributed in the solution more inseparable. When the acid gas is introduced into the amine solution at the same flow rate, the lower amine concentration is more conducive to contact between acid gas molecules and amine molecules. Thus, the actual experimental results show that

the acid gas load of the amine solution decreases when the amine concentration increases. Apparently, when the amine concentration is higher, the water content will be correspondingly lower, and the viscosity value of the solution will be greater, thus increasing pipeline resistance and energy consumption. However, if the MDEA concentration is too low, the circulation volume will increase; therefore, the desulfurization solvent generally employed industrially is a 40% MDEA aqueous solution.

**Table 3.** Experimental results of acid gas absorption by TBEE solution at different temperatures and concentrations.

Temperature (°C)	TBEE Concentration (%)	$x_{H_2S}$ (g/mL)	$x_{CO_2}$ (g/mL)	$L_{H_2S}$	$L_{CO_2}$	S
30	10	0.04165	0.0262808	0.073755	0.055776	15.85
30	20	0.08285	0.0521248	0.07337	0.055344	15.89
30	30	0.11625	0.0733824	0.06864	0.051936	15.84
30	40	0.15265	0.0976612	0.067595	0.05184	15.63
30	50	0.18995	0.121394	0.067265	0.051552	15.65
40	10	0.04045	0.0255164	0.07304	0.049056	15.85
40	20	0.0765	0.0482664	0.06842	0.046128	15.85
40	30	0.11095	0.0702156	0.070235	0.047232	15.80
40	40	0.1478	0.0934752	0.06798	0.046416	15.81
40	50	0.18435	0.1169532	0.068035	0.04656	15.76
50	10	0.03825	0.0242788	0.06908	0.04056	15.75
50	20	0.07065	0.0452452	0.066385	0.039264	15.61
50	30	0.10175	0.065338	0.06578	0.038928	15.57
50	40	0.13505	0.0869232	0.06391	0.038016	15.54
50	50	0.1716	0.1101464	0.061215	0.036384	15.58
60	10	0.03395	0.0217308	0.064075	0.03792	15.62
60	20	0.06365	0.0409136	0.06325	0.037536	15.56
60	30	0.09175	0.0592592	0.060225	0.035712	15.48
60	40	0.12225	0.0792064	0.058135	0.034752	15.43
60	50	0.15055	0.0978068	0.05742	0.034416	15.39

Comparing the data in Tables 2 and 3, it can be found that in MDEA and TBEE,  $x_{H_2S}$ ,  $x_{CO_2}$ ,  $y_{H_2S}$ ,  $y_{CO_2}$  and S vary with temperature and concentration, and the variation law of temperature and concentration is consistent; that is, with the increase in amine solution temperature, both  $x_{H_2S}$  and  $x_{CO_2}$  decrease; with the increase in amine concentration, both  $x_{H_2S}$  and  $x_{CO_2}$  increase. The amplitude of the selectivity factor S tends to decrease with the increase in temperature and amine concentration, but the decrease is not large. This indicates that low temperature and low concentration are beneficial to the selective absorption of  $H_2S$  by the amine solution, and the selectivity is not greatly affected by temperature. Comparing the acid gas load and selectivity of the TBEE and MDEA solutions at the same temperature and the same concentration, the selective removal of  $H_2S$  by TBEE is much greater than that of MDEA, and the acid gas load of TBEE is also greater than that of MDEA. Surprisingly, TBEE exhibits good  $H_2S$  absorption selectivity at different temperatures and concentrations, which is comparable to the data reported by using protic ionic liquids [31]. The effect of an MDEA aqueous solution on absorbing  $H_2S$  and  $CO_2$  in tail gas was investigated to compare the desulfurization and decarbonization performance of different amine formulations under similar reaction conditions. The corresponding operating parameters used in the MDEA solutions are shown in Table S2, and the results of its absorption performance are depicted in Table 4.

**Table 4.** Experiment results of H<sub>2</sub>S and CO<sub>2</sub> removal rate in MDEA aqueous solution.

Entry	40% MDEA + 60% H <sub>2</sub> O					
	Raw Gas		Purified Gas		H <sub>2</sub> S Removal Rate%	CO <sub>2</sub> Co-Absorption Rate%
	H <sub>2</sub> S%	CO <sub>2</sub> %	H <sub>2</sub> S mg/m <sup>3</sup>	CO <sub>2</sub> %		
1	2.01	30.45	366.86	25.66	98.37	23.41
2	1.97	30.43	359.74	25.19	98.34	25.17
3	2.00	30.50	374.23	25.60	98.33	23.82
4	2.05	30.46	398.27	25.96	98.29	22.28
5	2.04	30.50	378.24	25.85	98.36	22.87
Average	2.01	30.47	375.47	25.65	98.33	23.52

Reaction conditions: Packing height 1.0 m, lean liquid temperature 39.5 °C, feed gas flow 400 L/h, solution circulation volume 2.0 L/h, gas-liquid ratio 200.

As shown in Table 4, under the reaction conditions of a packing height of 1.0 m, gas-liquid ratio of 200, H<sub>2</sub>S content about 2.0%, and CO<sub>2</sub> content about 30% in the raw gas, the average H<sub>2</sub>S content in the purified gas treated with the MDEA aqueous solution was 375.47 mg/m<sup>3</sup>, and the average co-absorption rate of CO<sub>2</sub> was 23.52% (please see Tables S3–S5 for detailed data on reaction conditions and results of absorption of H<sub>2</sub>S and CO<sub>2</sub> by MDEA, TBEE, and their mixture). This indicates that the MDEA aqueous solution has poor selective removal of H<sub>2</sub>S at low pressure.

Subsequently, the desulfurization performance of TBEE was also investigated, with the results shown in Table 5. Under similar conditions to hydrogenated tail gas, the co-absorption rate of CO<sub>2</sub> was only 20.38%, which was 13.35% lower than that of MDEA. The H<sub>2</sub>S in purified gas was only 30.20 mg/m<sup>3</sup>, which was 91.96% lower than that of MDEA, and the performance was comparable to that of similar sterically hindered amines. The experimental results show that TBEE has good selectivity and a high ability to absorb H<sub>2</sub>S, which further certifies the results obtained in Tables 2 and 3.

**Table 5.** Experiment results of H<sub>2</sub>S and CO<sub>2</sub> removal in TBEE aqueous solution.

Entry	40% TBEE + 60% H <sub>2</sub> O					
	Raw Gas		Purified Gas		H <sub>2</sub> S Removal Rate%	CO <sub>2</sub> Co-Absorption Rate%
	H <sub>2</sub> S%	CO <sub>2</sub> %	H <sub>2</sub> S mg/m <sup>3</sup>	CO <sub>2</sub> %		
1	2.08	30.29	27.04	25.17	99.88	24.90
2	2.01	29.21	32.49	25.23	99.86	20.54
3	2.03	29.55	37.06	26.00	99.84	18.65
4	2.11	30.17	25.72	26.70	99.90	18.24
5	2.10	30.41	28.71	26.67	99.88	19.28
Average	2.07	29.93	30.20	25.95	99.87	20.38

Reaction conditions: Packing height 1.0 m, lean liquid temperature 38.5 °C, feed gas flow 400 L/h, solution circulation volume 2.0 L/h, gas-liquid ratio 200.

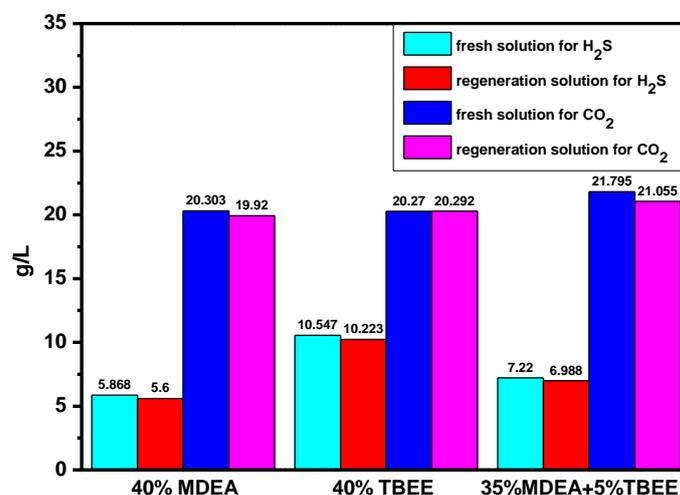
Considering the price of TBEE is higher than that of the commonly used MDEA, the desulfurization performance of the formula solution formed by adding TBEE to MDEA was subsequently studied, as shown in Table 6. Through the evaluation of the formula solution, it was found that after adding 5% TBEE to the 35% MDEA solution, the average co-absorption rate of CO<sub>2</sub> was 22.68%, which was still lower than that of the 40% MDEA solution, and the removal rate of H<sub>2</sub>S was as high as 99.79%, which can satisfy exhaust gas emission requirements. The results of the present study indicated that TBEE is also an excellent sterically hindered amine that can be further used to develop blended solvents, which is consistent with the conclusions reported in the literature by using MDEA-TBEE blended amines to selectively remove H<sub>2</sub>S from gas mixtures [23].

**Table 6.** Experiment results of H<sub>2</sub>S and CO<sub>2</sub> removal in mixed solution of TBEE and MDEA.

5% TBEE + 35% MDEA + 60% H <sub>2</sub> O						
Entry	Raw Gas		Purified Gas		H <sub>2</sub> S Removal Rate%	CO <sub>2</sub> Co-Absorption Rate%
	H <sub>2</sub> S%	CO <sub>2</sub> %	H <sub>2</sub> S mg/m <sup>3</sup>	CO <sub>2</sub> %		
1	1.96	30.98	47.18	26.35	99.79	22.55
2	2.02	30.5	44.19	25.71	99.80	23.43
3	1.92	30.42	47.53	25.86	99.78	22.42
4	2.02	30.6	46.79	26.01	99.80	22.59
5	2.02	30.59	45.3	26.05	99.80	22.39
Average	1.99	30.62	46.20	26.00	99.79	22.68

Reaction conditions: Packing height 1.0 m, lean liquid temperature 38.7 °C, feed gas flow 400 L/h, solution circulation volume 2.0 L/h, gas-liquid ratio 200.

Furthermore, an experimental study of solution regeneration was conducted. At the regeneration temperature, the solution was subjected to multiple absorption regeneration experiments to test the content of H<sub>2</sub>S and CO<sub>2</sub> in the rich solution after desulfurization of the fresh amine solution and compared with the solution after multiple regenerations. The content of H<sub>2</sub>S and CO<sub>2</sub> in the lean solution after multiple regenerations was analyzed to judge the regeneration performance of the solution. The experimental results are shown in Figure 2 (for more specific data, see Table S6). It can be seen from the data in Figure 2 that compared with the fresh solution, the H<sub>2</sub>S and CO<sub>2</sub> content in the rich solution after multiple regenerations had little change, and the H<sub>2</sub>S and CO<sub>2</sub> content in the lean solution after multiple regenerations was very low, indicating that after multiple cycles under this condition the TBEE solution still maintains its desulfurization performance, showing a good regeneration effect.

**Figure 2.** Comparison of absorption ability of fresh solution and regeneration solution.

In the process of alkanolamine desulfurization, the corrosive effect of the desulfurization solvent often causes liquid leakage in towers, pipelines, and containers of desulfurization units, resulting in the serious corrosion of equipment. Corrosion not only causes solvent loss, it also shortens the start-up cycle of the device and increases maintenance costs. Therefore, reducing the corrosiveness of the desulfurization solvent is of great significance for extending the service lifetime of equipment, ensuring the safe and smooth operation of the purification device, and reducing production costs. Subsequently, a static corrosion test was carried out to investigate the corrosion of carbon steel by TBEE; meanwhile, the corrosion ability of MDEA aqueous solution was also investigated, and the test data are shown in Figure 3 (please see Table S7 for reaction conditions and detailed data of corrosion testing). The average corrosion rate of the TBEE aqueous solution was 0.0221

mm/a, while the average corrosion rate of the MDEA aqueous solution was 0.0281 mm/a. The two solutions exhibited lower static corrosion rates, but TBEE exhibited a small but non-negligible anti-corrosion performance advantage, which implied a good potential for industrial applications.

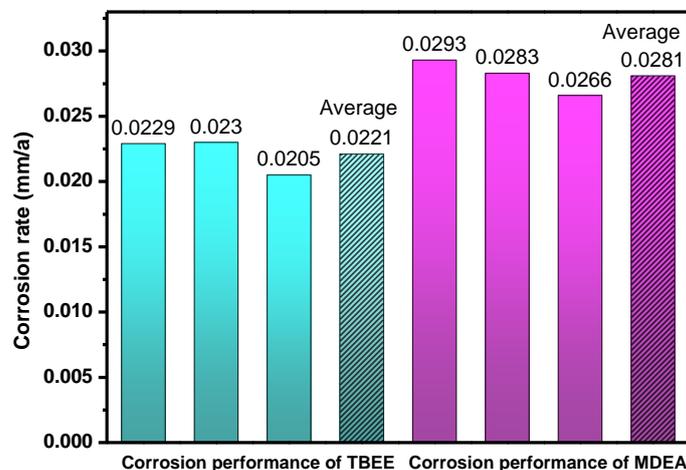


Figure 3. Corrosion rate performance of TBEE solvent system and MDEA aqueous solution.

## 5. Conclusions

In summary, the present work illustrates efficient secondary alkanolamines for selective H<sub>2</sub>S absorption from a mixed-gas stream. The absorption performance of MDEA and TBEE solutions was studied using an atmospheric packed column. In addition, the absorption properties of blended amines of MDEA and TBEE solutions were also verified. A series of absorption factors were investigated, and the experimental results showed that the H<sub>2</sub>S absorption selective factors were 3.88 and 15.81 using 40% methyldiethanolamine and 40% 2-tertiarybutylamino-2-ethoxyethanol at 40 °C, respectively, which indicated that the performance of the TBEE solution was better than the MDEA solution for selective H<sub>2</sub>S absorption of mixed acid gases. Happily, the blended MDEA and TBEE amines showed a 99.79% H<sub>2</sub>S removal rate and 22.68% CO<sub>2</sub> co-absorption rate, while 40% methyldiethanolamine alone had a 98.33 H<sub>2</sub>S removal rate and 23.52% CO<sub>2</sub> co-absorption rate. That is, the absorption performance of blended amines was better than that of the MDEA solution alone. Moreover, the corrosion performance of the amine solution is also a crucial factor that should be noted in industry application. Fortunately, the corrosion test demonstrated that the TBEE solution exhibited a 0.0221 mm/a corrosion rate, which was better than the 0.0281 mm/a obtained by MDEA solution. Accordingly, TBEE is an outstanding choice in selective H<sub>2</sub>S absorption, and its advantages in selective H<sub>2</sub>S absorption could have potential application in the industrial gas purification field. Although TBEE shows good performance and displays an important role in blended amine solutions, its application in industry still needs more experimental verification, and further research on the application of TBEE is in progress in our laboratory.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pr10091795/s1>; Table S1: Comparison of absorption effect between atmospheric pressure test device and industrial device; Table S2: Operating parameters for desulfurization performance evaluation; Table S3: Experiment results of MDEA aqueous solution to absorb H<sub>2</sub>S and CO<sub>2</sub>; Table S4: Experiment results of TBEE aqueous solution to absorb H<sub>2</sub>S and CO<sub>2</sub>; Table S5: Experiment results of absorption of H<sub>2</sub>S and CO<sub>2</sub> by mixed solution of TBEE and MDEA; Table S6: Comparison of absorption ability of fresh solution and regeneration solution; Table S7: Static corrosion rate data of TBEE solvent system and MDEA aqueous solution.

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