

# The Equilibrium Solubility of Carbon Dioxide in the Mixed Aqueous Solutions of Triisopropanolamine and Monoethanolamine in the Range 30-70 °C and Low Partial Pressures

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**ABSTRACT:** *The equilibrium solubility data of CO<sub>2</sub> in the various aqueous blends of triisopropanolamine (TIPA) + monoethanolamine (MEA) with the total alkanolamine concentration of 2 mole / dm<sup>3</sup> were measured at the temperatures of 30, 40, 50, 60 and 70 °C and CO<sub>2</sub> partial pressures below 100 kPa. The experiments were done in an atmospheric gas absorption system and the amount of absorbed CO<sub>2</sub> was measured with acidification method and by a graduated burette. The results indicate that the increase in the CO<sub>2</sub> partial pressure or the MEA ratio in the blended solvents increases the absorption capacity of the solutions and when the temperature is increased, the capacity decreases. Hence, one can use proper blends of TIPA+MEA to obtain acceptable absorption capacity and lower the regeneration cost and benefit from other useful properties of TIPA such as its low corrosivity and low degradation rate. Immersion corrosion tests carried out on stainless steel 304 coupons at 45 °C for 15 days in some blended solvents, in the presence or absence of dissolved CO<sub>2</sub>, showed no corrosion.*

**KEY WORDS:** *Carbon Dioxide, Alkanolamine, Triisopropanolamine, Monoethanolamine, Gas Absorption*

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## INTRODUCTION

The absorption of acidic gases such as CO<sub>2</sub> and H<sub>2</sub>S in alkali solutions is a usual and important industrial process especially in the sweetening of the natural gas and has been used for many years. Alkanolamine solutions, such as monoethanolamine (MEA) and methyldiethanolamine (MDEA), are the examples of the alkali solutions, used for such purposes. Triisopropanolamine (TIPA) as a tertiary amine, has not been used in the absorption of the acid gases. As a result of the high steric hindrance of TIPA, similar to other hindered amines, it can not easily react with CO<sub>2</sub>. Therefore, the strongly bonded carbamate compound production, is minimum and the solution can be regenerated easier and with lower energy consumption than unhindered alkanolamines [1,2,3]. Mixed amines in comparison with single amine systems, retain much of the reactivity of the primary or secondary amines at similar or reduced circulation rates and offer low regeneration costs similar to those of tertiary amines. Other suitable attributes of the amine blends include the low corrosivity and low degradation rates [1,4].

Solubility data are very important in the design of industrial gas absorption units and hence, many researchers have concentrated on this field. For example, Austgen et al. [5] measured the solubility of CO<sub>2</sub> in the aqueous mixtures of MDEA with MEA or DEA (Diethanolamine) at 40 and 80 °C. Jou et al. [6] measured the equilibrium solubility of H<sub>2</sub>S and CO<sub>2</sub> in the various Triethanolamine (TEA) solutions at 25, 50, 75, 100 and 125 °C. Similar studies have been done by Xu et al. [7], Liu et al. [8], Roberts and Mather [9], and Teng and Mather [10].

This paper reports the solubility data of CO<sub>2</sub> in the aqueous solutions of TIPA + MEA, in the various conditions of temperature, concentrations of TIPA and MEA, and CO<sub>2</sub> partial pressures below 100 kPa. Results of some corrosion tests are also reported.

## EXPERIMENTAL

### Chemicals

The solutions were prepared using distilled water. MEA was from Riedel – De Haen (Germany) with 99 % purity. TIPA was from Aldrich Company (USA) with 95 % purity and was used without purification. CO<sub>2</sub> was from Ehterami Company (Iran) with minimum purity of

98 % and Argon was from Roham Gas Company (Iran) with certified purity of 99.999 %.

### Apparatus and Procedures

The solubility data were measured using an atmospheric pressure apparatus (Fig. 1) similar to the one used by Xu et al. [7] and Liu et al. [8]. The temperature in the reactor was fixed within  $\pm 0.1$  °C by a temperature controller (Jumo iTron 04, Germany), which was adjusting the temperature in a thermostated water bath. The proper flows of CO<sub>2</sub> and Argon were adjusted within  $\pm 0.3$  % by Flow Controllers (Supelco – VCD 1000) and then were mixed in a mixing tube to make the proper CO<sub>2</sub> partial pressures. The total gas flow in all experiments was about 150 cm<sup>3</sup> / min. The resulting gas stream passed through a saturator at room temperature and, the saturated gas stream was bubbled into the alkanolamine solution.

The outlet gas, passed through a room temperature condenser to return the evaporated water into the cell. To ensure that equilibrium had been reached, the experimental time was kept at least 4 h prior to sampling the liquid phase. The CO<sub>2</sub> content in the liquid phase was determined by addition of an excess amount of phosphoric acid on the samples and then measurement of the evolved volume of CO<sub>2</sub> by a graduated burette [7,8]. Determination of CO<sub>2</sub> loading in the amine solution had an error of  $\pm 5$  %. In this work, the partial pressure of

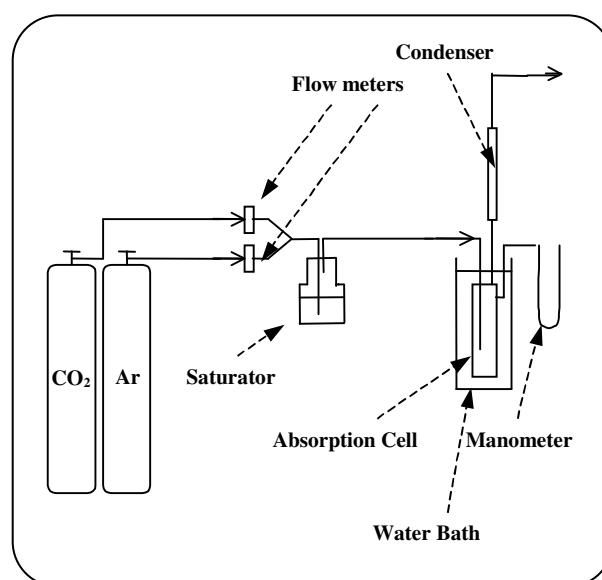


Fig. 1: Schematic of atmospheric pressure gas absorption system

water above the alkanolamine solution was determined using Raoult's law, and the vapor pressures of TIPA and MEA were neglected. The experiments were carried out in the temperature range between 30 °C to 70 °C, the total amine (TIPA + MEA) concentration of 2 mole / dm<sup>3</sup> and CO<sub>2</sub> partial pressures below 100 kPa. Fig. 2 compares our CO<sub>2</sub> solubility data in the 15.3 wt % aqueous solutions of MEA at 40 °C, with those reported previously [11-14].

The corrosion studies were carried out on stainless steel 304 coupons according to ASTM G31 [15] with and without dissolved CO<sub>2</sub>. In the absence of dissolved CO<sub>2</sub>, the alkanolamine solution was refluxed in contact with metal coupon. The reflux column had been equipped with an atmospheric seal. In the presence of dissolved CO<sub>2</sub>, after 1 h CO<sub>2</sub> bubbling into the solution, the corrosion cell was sealed to keep the CO<sub>2</sub> partial pressure above the solution. The temperature was fixed at 45 ± 0.1 °C using the temperature controller and the water bath. The corrosion test duration time was about 15 days. Before the test, the coupons were treated using sand paper, washed by detergent then by acetone and finally were dried. After performing the tests, the coupons were washed and dried again. The corrosion rates were calculated using the equation:

$$\text{Corrosion Rate} = (K.W) / (A.t.D) \quad (1)$$

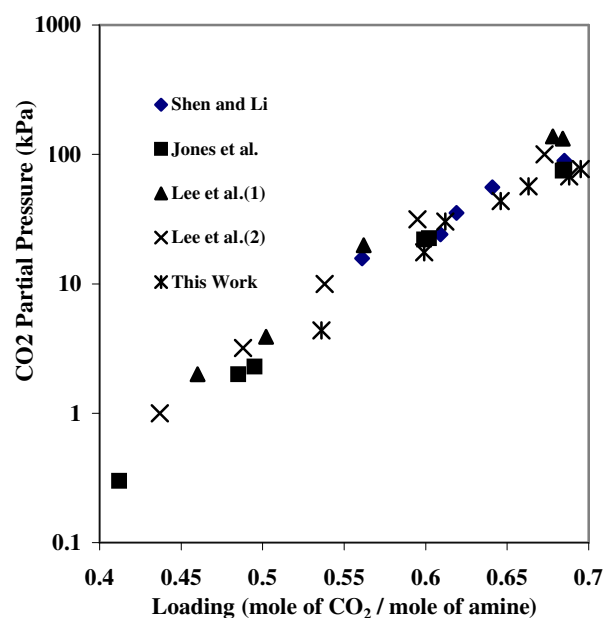
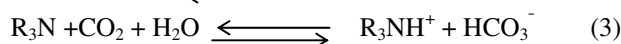
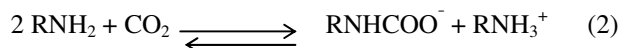


Figure 2. Comparison of CO<sub>2</sub> solubility in 15.3 wt% MEA aqueous solution at 40 °C, between our data and those reported previously:  $\diamond$ , Shen and Li;  $\square$ , Jones et al.;  $\triangle$ , Lee et al. (1);  $\times$ , Lee et al. (2);  $*$ , This work

where K is a constant and has a value of  $1 \times 10^4 \times D$ , t is time of exposure in hours to the nearest 0.01 h, A is area in cm<sup>2</sup> to the nearest 0.01 cm<sup>2</sup>, W is mass loss in g to nearest 1 mg (corrected for any loss during cleaning) and D is density in g/cm<sup>3</sup>, and the corrosion rate is in g/m<sup>2</sup>.h.

## RESULTS AND DISCUSSION

The experimental results on CO<sub>2</sub> equilibrium absorption are shown in Table 1. In this table, P<sub>CO<sub>2</sub></sub> is CO<sub>2</sub> partial pressure in kPa and  $\alpha_{\text{CO}_2}$  is CO<sub>2</sub> loading that is, moles of absorbed CO<sub>2</sub> per one mole of amine. Figures 3 and 4 show the CO<sub>2</sub> equilibrium absorption data in various TIPA + MEA solutions at 30 °C and 70 °C, as two examples. In all diagrams the vertical axis is CO<sub>2</sub> partial pressure in kPa and in logarithmic scale, and horizontal axis is CO<sub>2</sub> loading. From these figures it can be seen that increasing the MEA / TIPA ratio, increases the CO<sub>2</sub> loading. According to the equation 2, this is due to the strong carbamate bond formation, which forces the system to absorb more CO<sub>2</sub>. But according to equation 3, the production of carbamate between R<sub>3</sub>N and CO<sub>2</sub>, is impossible or difficult which is due to high steric hindrance around nitrogen atom of R<sub>3</sub>N. RNH<sub>2</sub> is a primary amine like to MEA, and R<sub>3</sub>N is a tertiary one like to TIPA.



The total absorption capacity of CO<sub>2</sub> also decreases as the temperature increases as shown in Figure 5, for an aqueous solution of TIPA (0.5 mole / dm<sup>3</sup>) + MEA (1.5 mole / dm<sup>3</sup>), as an example. This is because of decreasing the physical solubility of the gases with the increase in temperature. In the CO<sub>2</sub> absorption process, it should be noted that, the chemical reaction takes place after physical dissolution of CO<sub>2</sub>. This figure also shows that increasing the temperature decreases the CO<sub>2</sub> partial pressure, which is due to an increase in the water vapor pressure in the absorption cell, and this, decreases the CO<sub>2</sub> distribution from total pressure in the absorption cell. This can explain a small part of the decreasing the  $\alpha_{\text{CO}_2}$  with the increase in temperature. Fig. 3-5 also show the increasing CO<sub>2</sub> loading with increasing its partial pressure above the absorbing solution. Fig. 6 compares the CO<sub>2</sub> equilibrium absorption capacity of TIPA solution with that of 2-Amino-2-methyl-1-propanol (AMP) [10], MDEA [7] and

Table 1: Experimental results on CO<sub>2</sub> equilibrium absorption

T	$\alpha_{CO_2}$	$P_{CO_2}$	T	$\alpha_{CO_2}$	$P_{CO_2}$	T	$\alpha_{CO_2}$	$P_{CO_2}$
TIPA 2M			60	0.255	38.42	40	0.779	75.36
30	0.149	15.7	60	0.287	51.14	50	0.5	14.09
30	0.224	31.34	60	0.305	63.94	50	0.545	28.27
30	0.335	46.99	70	0.168	10.73	50	0.58	42.37
30	0.437	62.84	70	0.189	21.47	50	0.614	56.43
30	0.501	78.42	70	0.209	32.19	50	0.632	70.39
40	0.117	15.16	70	0.218	42.92	60	0.444	12.79
40	0.188	30.33	70	0.239	53.66	60	0.509	25.61
40	0.231	46.12	TIPA 1M + MEA 1M			60	0.54	38.54
40	0.269	61.39	30	0.575	15.63	60	0.552	51.31
40	0.301	76.1	30	0.62	31.19	60	0.574	64.07
50	0.127	14.08	30	0.688	46.77	70	0.38	10.72
50	0.176	28.18	30	0.715	62.36	70	0.422	21.42
50	0.189	42.18	30	0.759	77.95	70	0.44	32.08
50	0.214	56.43	40	0.417	15.29	70	0.463	42.73
50	0.224	70.55	40	0.488	30.52	70	0.502	53.36
60	0.119	12.91	40	0.554	45.69	MEA 2M		
60	0.132	25.8	40	0.561	60.82	30	0.757	15.64
60	0.143	38.39	40	0.597	75.97	30	0.808	31.27
60	0.149	51.01	50	0.399	14.15	30	0.852	47.13
60	0.181	63.62	50	0.45	28.28	30	0.878	62.77
70	0.06	10.73	50	0.466	42.4	30	0.911	78.34
70	0.079	21.45	50	0.5	54.41	40	0.689	15.11
70	0.087	32.14	50	0.524	70.69	40	0.788	30.17
70	0.097	42.79	60	0.337	12.8	40	0.804	45.2
70	0.113	53.49	60	0.377	25.56	40	0.815	60.23
TIPA 1.5M + MEA 0.5M			60	0.397	38.3	40	0.842	75.23
30	0.355	15.66	60	0.416	51.05	50	0.686	14.2
30	0.463	31.3	60	0.443	64.02	50	0.729	28.36
30	0.525	49.29	70	0.264	10.76	50	0.753	42.47
30	0.588	62.58	70	0.313	21.51	50	0.764	56.55
30	0.695	79.35	70	0.324	32.25	50	0.771	70.63
40	0.287	15.35	70	0.364	42.98	60	0.556	12.8
40	0.345	30.63	70	0.374	53.58	60	0.616	25.55
40	0.386	46	TIPA 0.5M + MEA 1.5M			60	0.695	38.25
40	0.433	61.2	30	0.669	15.66	60	0.708	50.95
40	0.461	76.41	30	0.755	31.29	60	0.723	63.49
50	0.26	14.21	30	0.794	47.05	70	0.457	10.67
50	0.301	28.36	30	0.818	62.67	70	0.557	21.32
50	0.328	42.45	30	0.859	78.37	70	0.615	31.93
50	0.373	56.38	40	0.592	15.06	70	0.643	42.47
50	0.389	70.33	40	0.666	30.08	70	0.701	53
60	0.21	12.65	40	0.714	45.16			
60	0.246	25.49	40	0.733	60.37			

 $\alpha_{CO_2}$ : mole of absorbed CO<sub>2</sub> per one mole of amine in solution $P_{CO_2}$ : CO<sub>2</sub> partial pressure (kPa)

T: temperature (°C)

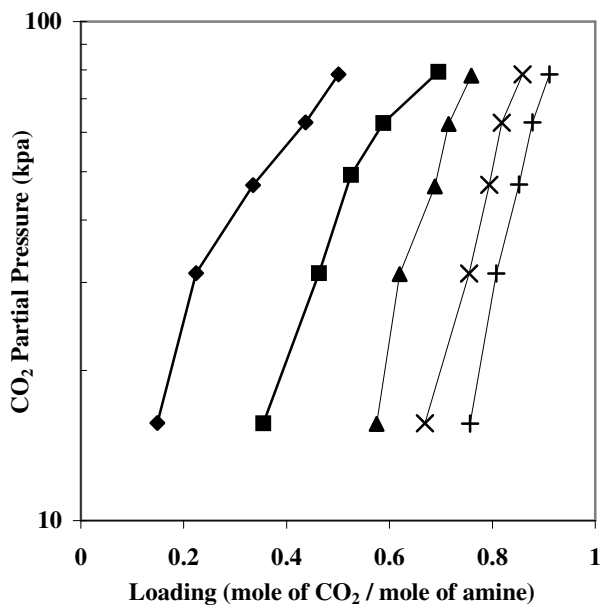


Fig. 3:  $CO_2$  partial pressure vs. its loading in various TIPA + MEA aqueous solutions at 30 °C:  $\blacklozenge$ , TIPA (2 mole /  $dm^3$ );  $\blacksquare$ , TIPA (1.5 mole /  $dm^3$ ) + MEA (0.5 mole /  $dm^3$ );  $\blacktriangle$ , TIPA (1 mole /  $dm^3$ ) + MEA (1 mole /  $dm^3$ );  $\times$ , TIPA (0.5 mole /  $dm^3$ ) + MEA (1.5 mole /  $dm^3$ );  $+$ , MEA (2 mole /  $dm^3$ )

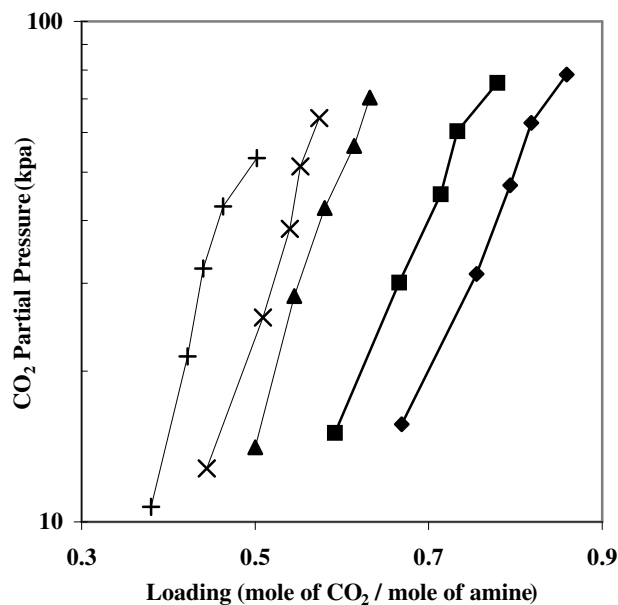


Fig. 5:  $CO_2$  partial pressure vs. its loading at various temperatures in aqueous solution of TIPA (0.5 mole /  $dm^3$ ) + MEA (1.5 mole /  $dm^3$ ):  $\blacklozenge$ , 30 °C;  $\blacksquare$ , 40 °C;  $\blacktriangle$ , 50 °C;  $\times$ , 60 °C;  $+$ , 70 °C

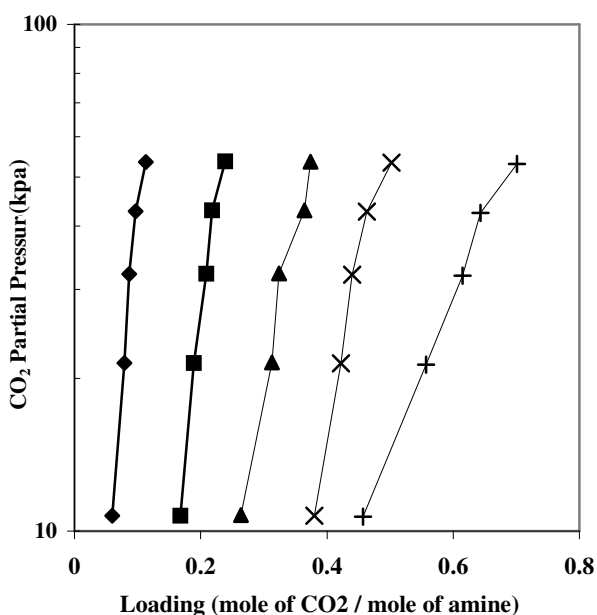


Fig. 4:  $CO_2$  partial pressure vs. its loading in various TIPA + MEA aqueous solutions at 70 °C:  $\blacklozenge$ , TIPA (2 mole /  $dm^3$ );  $\blacksquare$ , TIPA (1.5 mole /  $dm^3$ ) + MEA (0.5 mole /  $dm^3$ );  $\blacktriangle$ , TIPA (1 mole /  $dm^3$ ) + MEA (1 mole /  $dm^3$ );  $\times$ , TIPA (0.5 mole /  $dm^3$ ) + MEA (1.5 mole /  $dm^3$ );  $+$ , MEA (2 mole /  $dm^3$ )

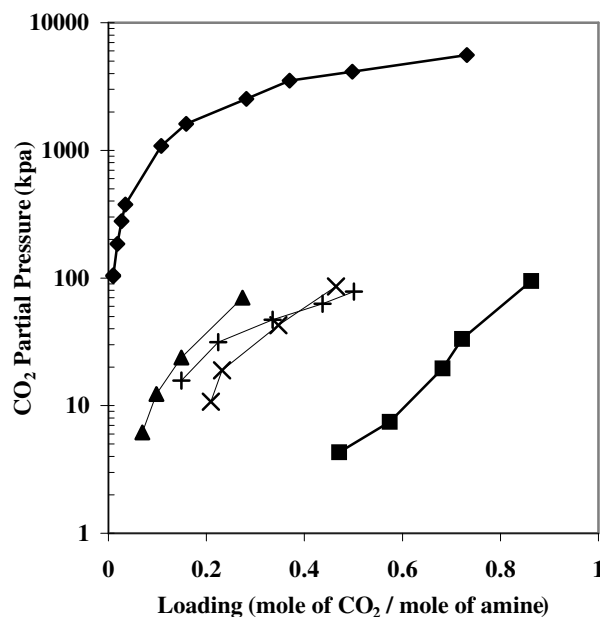


Fig. 6: Comparison of the  $CO_2$  equilibrium absorption capacity of TIPA with some of those reported previously:  $+$ , This work: aqueous TIPA 2M, 303.15 K;  $\times$ , Xu et al.: aqueous MDEA 3.04M, 328 K [7];  $\blacktriangle$ , Xu et al.: aqueous MDEA 3.04M, 343 K [7];  $\blacksquare$ , Teng and Mather: aqueous AMP 3.43M, 323.15 K [10];  $\blacklozenge$ , Roberts and Mather: Sulfinol 99%, 313.15 K [9]

Sulfinol [9]. It shows that in the experimental conditions, the capacity of MDEA solution is approximately similar to the TIPA solution, while AMP, at nearly similar partial pressures, has more equilibrium capacity than TIPA and Sulfinol at higher partial pressures, has lower or the same capacity.

Table 2 shows the results of the immersion corrosion tests after about 15 days exposure time, for amine solutions of TIPA (2 mole / dm<sup>3</sup>), TIPA (1 mole / dm<sup>3</sup>) + MEA (1 mole / dm<sup>3</sup>) and MEA (2 mole / dm<sup>3</sup>) at 45 °C on stainless steel 304 coupons. The results show no corrosivity on this alloy, with and without dissolved CO<sub>2</sub> in the solution, but to obtain more useful operational results, the tests should be done under conditions similar to the actual circumstances encountered in the absorption columns.

## CONCLUSIONS

The experimental results in temperature range from 30 °C to 70 °C and CO<sub>2</sub> partial pressures below 100 kPa in various TIPA + MEA blends, show that increasing the CO<sub>2</sub> partial pressure, increases the absorption capacity of the solutions. TIPA (2 mole / dm<sup>3</sup>) solution especially at high temperatures, has relatively low CO<sub>2</sub> absorption capacity, but replacing some TIPA with MEA and decreasing the temperature, increases the CO<sub>2</sub> absorption capacity to an acceptable extent. Hence, with proper blends of TIPA + MEA, we can benefit from the useful properties of TIPA blends such as low regeneration costs, low corrosivity, and low degradation rate, which are

**Table 2: Results of immersion corrosion tests at 45 °C and 15 days exposure time**

Metal coupon	Solution	Corrosion rate (g / m <sup>2</sup> . h)	
		With CO <sub>2</sub>	Without CO <sub>2</sub>
Steel-304	TIPA (2 mole / dm <sup>3</sup> )	Undetectable	Undetectable
Steel-304	TIPA (1 mole / dm <sup>3</sup> ) + MEA (1 mole / dm <sup>3</sup> )	Undetectable	Undetectable
Steel-304	MEA (2 mole / dm <sup>3</sup> )	Undetectable	Undetectable

important industrial problems.

Also, TIPA (2 mole / dm<sup>3</sup>), TIPA (1 mole / dm<sup>3</sup>) + MEA (1 mole / dm<sup>3</sup>) and MEA (2 mole / dm<sup>3</sup>) solutions at 45 °C have no corrosivity on stainless steel 304 in the absence or presence of CO<sub>2</sub> after 15 days exposure time. Therefore, ST-304 may be a suitable structural material for industrial units such as boilers and absorption columns, and the amines mentioned may probably be used as corrosion inhibitors in these units. However, to obtain more useful operational results, the tests should be done under conditions similar to the actual circumstances encountered in the absorption columns.

## Acknowledgements

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## Nomenclature

A	area (cm <sup>2</sup> )
AMP	2-amino-2-methyl-1-propanol
ASTM	American society for testing and materials
D	density (g / cm <sup>3</sup> )
DEA	Diethanolamine
K	constant (g / m <sup>2</sup> .h) or Kelvin
M	mole / dm <sup>3</sup>
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
P <sub>CO2</sub>	CO <sub>2</sub> partial pressure (kPa)
ST-304	stainless steel 304
T	temperature (°C)
t	time of exposure (h)
TEA	Triethanolamine
TIPA	Triisopropanolamine
W	mass loss (g)
α <sub>CO2</sub>	CO <sub>2</sub> loading (mole of CO <sub>2</sub> / mole of amine)

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