



Investigation of Sulfolane Degradation in Aqueous Alkanolamine Solutions Under the Stripping Operational Condition

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Abstract

The measure of stability of sulfolane (SFL) in aqueous alkanolamine solution was investigated. For this purpose, degradation of SFL was experimentally studied under the stripping operational condition ($T = 130\text{ }^{\circ}\text{C}$). The experiments were divided into two general categories: (1) aqueous solution of SFL with and without presence of oxygen to receive a sense of thermal and oxidative SFL degradation; (2) aqueous solution of MDEA/PZ/SFL loaded by hydrogen sulfide and carbon dioxide (both gas-loadings were set to be 0.25 to roughly make a real condition). The results of the experiments showed that SFL resists thermal degradation, but in the presence of oxygen and temperatures of $130\text{ }^{\circ}\text{C}$ which is in accordance with the desorption operational conditions, it would be prone to degradation to anions such as sulfite, sulfate and thiosulfate.

Keywords Alkanolamine solution · Hybrid solvent · Oxidative degradation · Sulfolane

1 Introduction

Processes that used mixed aqueous alkanolamine as a chemical solvent and a SFL or thiodiglycol as a physical one are known as hybrid processes. Sulfinol process launched by Shell in the 1960s [1] could be mentioned as an example of hybrid process. In the early sulfinol solvent, the mixture of DIPA, SFL and water named Sulfinol-D was used in process. Later DIPA was replaced by MDEA and was termed Sulfinol-M and then by adding piperazine (PZ) as an accelerator (especially for

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CO₂) it was known as Sulfinol-X. SFL concentration reached may even be as high as 60 % in Shell process when is used for H₂S and CO₂ removal from raw natural gas condensate [2].

A quick literature survey showed that hybrid solvents with SFL + alkanolamine mixture formulation have been largely used for acid gases solubility. In 2016, Dash and Bandyopadhyay [3] presented that the addition of SFL can improved CO₂ absorption capacity of aqueous MDEA/PZ solution. Feng et al. [4] investigated the simultaneous removal of H₂S and sulfur compounds from liquefied petroleum gas. Ghanbarabadi et al. [5] reported that Sulfinol-M has 10–25 % less energy required in regeneration step compared to amine solution. Torabi et al. [6] optimized SFL concentration in the Sulfinol-M using simulation. Rostami and Tavan [7] for the industrial gas sweetening unit of NIGC, successfully substituted hybrid solution (MDEA/PZ/SFL) for aqueous solution of MDEA/PZ. They experimentally showed that addition of SFL in aqueous solution of MDEA/PZ has some significant impact on the quality of process including: (1) when SFL concentration increased to 12 wt %, the mercaptane concentration in natural gas stream is reduced from 1300 ppm to 776 ppm; (2) addition of SFL reveals higher solubility of hydrocarbon which verifies the result reported by Bedell and Miller [8]; (3) increase in SFL concentration results in lower regeneration heat duty as confirmed by Dash and Bandyopadhyay [3] as well as Zong and Chen [9]; (4) foaming and corrosion are increased with addition of SFL.

Pure SFL under standard operational condition seemed to be stable and non-corrosive, however in case of SFL contaminated by oxygen, at high temperature and in the presence of water, it may lead to decomposition and formation of corrosive by-products [10]. Kus et al. [11] have shown that oxygen above 0.5 % and water above 3 % can accelerate SFL degradation and production of acidic corrodents. However, SFL degradation knowledge should be considered at special condition of desorption of sweetening unit to reach a cause of foaming and corrosion increasing with SFL,s addition. Considering the fact that the temperature of the amine solutions in regeneration tower rises to about 120–140 °C, it may suffer from decomposition, evaporation and degradation at such a high temperature and it may even occasionally experience foaming [1, 12]. In this work, to address the foaming and corrosion of solvent containing MDEA/PZ with addition of SFL [7], desorption operating conditions was simulated in the laboratory to get a sense of degradation behavior of this type of solvent.

Oxidative and thermal degradation of solvent composite are two important sources of undesirable compounds which lead to increasing of corrosion and foaming. Adding SFL may increase corrosion and foaming through two scenarios: the first one, it may refer to degradation of SFL in presence of oxygen and the second scenario may be addressed to raising the oxygen solubility in SFL-contained solvents compared to the aqueous solvent. This work aims to address the first scenario and investigate the stability and degradation of SFL at temperature of desorption tower and presence of oxygen. Two types of experiments were designed under the operating conditions of the desorption tower: (1) degradation of 15 wt % of aqueous SFL solution in both the presence and absence of oxygen at 130 °C in one batch (SFL solution); (2) degradation of mixed solvent (including MDEA, PZ and SFL)

loaded by acid gases in the presence and absence of oxygen at 130 °C in one batch to make a real industrial condition. In fact by removing amines and acid gases in first test, only the degradation of SFL has been studied. By information about the quality and quantity of only SFL degradation received from the first test, in the second test a real solution was investigated. In the next sections of this study, the details of the experiments will be described and the results will be presented and explained.

Moreover, owing to this fact, besides SFL, there are three other components (namely H₂O, MDEA and PZ) in the system under study, the knowledge of the degradation behavior of MDEA and PZ in aqueous media may help us to achieve a proper interpretation of results. The amine degradation includes a series of irreversible reactions which are responsible for amine elimination from gas processing and decrease solvent efficiency and are generally divided into two types: (1) carbamate polymerization degradation and (2) oxidative degradation. The degradation caused by polymerization reactions are dominant at temperatures between 100 °C and 200 °C (under the conditions of the desorption tower). The mechanism of this kind of degradation is in a way that a carbamate anion is converted into oxazolidine and consequently it is prone to be imposed to forms dimer, trimer or even polymer [13–19]. Primary amines are more easily involved in this kind of degradation due to the fact that they easily contribute in the formation of carbamate, secondary amines such as DEA and PZ, with a rather slow rate in comparison with MEA, are also involved in this kind of polymeric degradation reaction. The oxidative degradation of the amines results from the presence of oxygen [20, 21], the presence of active radicals, some metal ions [22–26], sulfur oxides [27, 28] and nitrogen [29–31]. Oxidation of solvent species, not only removes amine from gas processing, but also by converting it to the other species, can lead to higher amount of heat-stable salts and an increase in corrosion rate [32]. Therefore, degradation and corrosion are two interconnected phenomena can increasingly aggravate each other.

The main products of oxidative degradation of amines are acetates, formates, oxalates, succinates and glycolates which can cause corrosion of the refinery equipment [33].

2 Experiments

2.1 Materials and Compounds

The chemicals used in this work are: (1) methyldiethanolamine with ≥ 99 % purity by weight (wt %) prepared by Sigma-Aldrich and CAS (Chemical Abstract Service) Registry number [105-59-9]; (2) piperazine from Sigma-Aldrich with a purity of ≥ 99 % wt % and CAS Registry number [110-85-0]; (3) sulfolane from Sigma-Aldrich with CAS Registry number [126-33-0] and a purity of ≥ 99 wt % containing 0.2 wt % of water; (4) the distilled water which was deionized twice by ion-exchange resin at the Research Institute of Petroleum Industry (RIPI) and the total dissolved substance (TDS) was measured as an impurities less than 10 ppm_w (part per million mass); (5) hydrogen sulfide gas with CAS Registry number [7783-06-4] with ≥ 99.95 mol % purity from ROHAM Company; (6) carbon dioxide from ROHAM Company with CAS Registry

number [124-38-9] with a purity of 99.5 mol %. All materials used in this work accompanied with purity, preparation and purification methods are summarized in Table 1. It should be noted that the materials purchased were used without any further purification.

2.2 Experimental Design

All experimental tests were carried out in the operating conditions of the desorption tower (130 °C) (Fig. 1). Due to lack of laboratory equipments to control the operational conditions, the batch reactors with static method were used. The solvent degradation apparatus with a batch method includes the following parts: needle valves v1 to v4 that connect the cylinder to the system. Needle valve v5 for vacuum of cylinder and system lines. The needle valves v6 and v7 connect the cylinders to the gas sample and the gas sample to the reactor. Needle valves v9, v12 and v8 are used for draining and washing the reactor as well as vacuum. Needle valve v11 is used to inject solvent into the reactor and v10 for sampling. Electrical heating system, GMH 3750 temperature sensor, located inside the Thermo-well of the equilibrium cell and a digital magnetic stirrer heater, carbon dioxide gas cylinder, air gas cylinder for oxygen supply, hydrogen sulfide gas cylinder, nitrogen gas cylinder, pressure sensors (P1 and P2) of Digi gauge (Roto therm) in the range of 0–10 bar that, respectively, determine the pressure of the gas sample and reactor. The reactor volume is 1800 cc and all the connecting pipes used in this work were stainless steel 316 (SS-316) with a size of 1.8 and 1.4 inches. Sampling line with a size of 1.8 was used due to control the sampling rate and up to 2 cm from the bottom of the reactor was covered. After sampling of solution at different times, the concentration of anions and neutral species, including SFL and amines in the system were detected at any moment by gas chromatography and ion chromatography. The CP-3800 model of the VARIAN brand of gas chromatography instrument used which has a 1041 split/splitless inlet. The injector temperature is set at 320 °C. The flame ionization detector (FID) was used in this method and its temperature is set at 300 °C. The DB-Wax column of the J & W Scientific Company with a length of 15 m and a diameter of 0.53 mm and a film thickness of 1 µm was used. In this method, the temperature was programmed as follows: first, the oven temperature was set at 90 °C and kept for 3 min at this temperature, then with a rate of 60°/min the temperature went up to 150 °C and remained at this temperature for 5 min. This temperature program has performed the good separation for mentioned species in the column, and then to remove all impurities, the oven temperature was set at 230 °C with a rate of 60°/min and remained at that temperature for 20 min to ensure that all contaminants are removed from the column. An external standard method was used for calibration and the standard samples were synthesized in the laboratory. The uncertainty of concentration of neutral species and also anions were obtained from the standard deviation of repetitions.

Table 1 Specification of the provided or purchased materials, as well as their analysis methods and purification

Chemical substance	Molecular formulas/ molecular weigh (g.mol ⁻¹)	Identification code	Purity	Analysis method	Purification method	Supplier
Hydrogen sulfide	34.08/(H ₂ S)	7783-04-4	% 99.95 ≤	GC ^a	Without purification	Roham gas Company
Carbon dioxide	44.01/(CO ₂)	124-38-9	% 99.5 ≤	GC ^a	Without purification	Roham gas Company
Methyl diethanolamine	119.16/(C ₃ H ₇ O ₂ N)	105-59-9	% 99.0 ≤			Sigma-Aldrich Company
Sulfolane	120.17/(C ₄ H ₈ O ₂ S)	126-33-0	% 99.0 ≤	Karl Fischer titration ^b	12 h were kept under vacuum	Sigma-Aldrich Company
Piperazine	86.14/(C ₄ H ₈ N ₂)	110-85-0	% 99.0 ≤			Sigma-Aldrich Company
Distilled water has been deionized twice	18.015/(H ₂ O)	7732-18-5		Conductometer ^c	Ion-exchange resin	Research Institute of Petroleum Industry
Sodium carbonate	Na ₂ CO ₃ /(105.9884)	497-19-8	99.5–100.5 %	HPLC ^d		Riedel-de Haën Company
Sodium hydrogen carbon- ate	(84.007) NaHCO ₃	144-55-8	99.5 %	HPLC ^d		Merck Company

^aThe gas chromatography and its information are given by the manufacturer^bThe amount of water in SFL was reported 0.2 % by the manufacturer and this was confirmed by Carl Fisher's titration^cThe total amount of impurities in water was obtained less than 10 ppm by conductivity measurement^dHigh performance liquid chromatography technique performed by the manufacturer

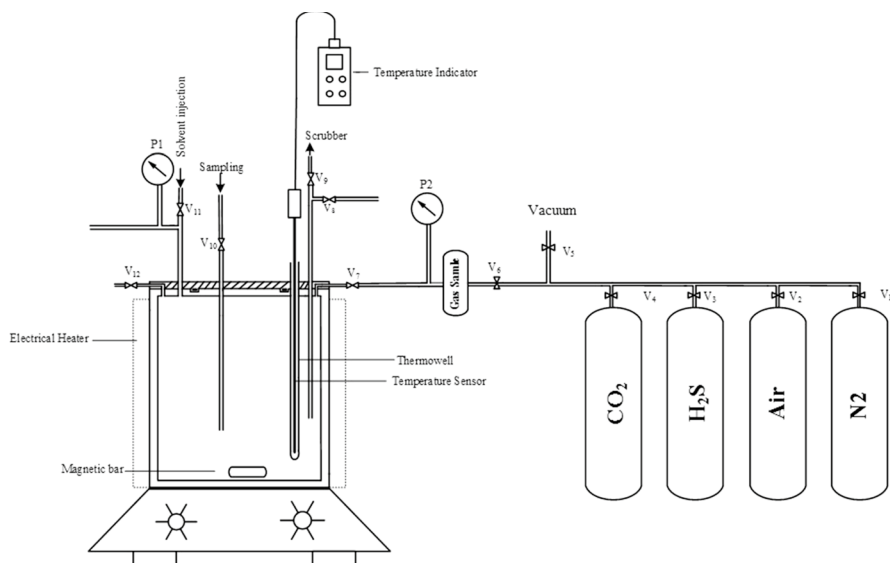


Fig. 1 Schematic of the designed system for measuring sulfolane and amine degradation

3 Results and Discussion

As explained in the introduction, the experiments were divided into two groups: the first one was performed with and without oxygen for aqueous 15 wt % SFL solution and the second one was performed with and without oxygen for solvent formulated with composition of 25.6 wt % MDEA, 1.3 wt % PZ and 35 wt % SFL. The initial partial pressure of oxygen in all experiments is 1 bar and because of high vapor pressure of aqueous solvents in such operational condition, all experiments have been carried out in laboratory batch system, so that the pressure of the solution after experiments is reduced due to oxygen consumption. The results of measurement of sulfite, sulfate and thiosulfate ions could be negligible for first group without the presence of oxygen meaning that no significant degradation was observed within a week, but the total concentration of sulfite, sulfate and thiosulfate anions for first group with presence of oxygen reached 182 ppm. The results of these experiments are presented in Table 2. Figure 2 shows the concentration changes of sulfite, sulfate and thiosulfate ions. Since this solvent has not been loaded by acid gases, the formation of these ions can only be due to the degradation of SFL. The synthesis and degradation pathway of SFL is shown in Fig. 3. In the synthesis pathway, sulfur dioxide reacts with butadiene (cheletropic reaction) and is converted into an intermediate product that is subsequently hydrogenated using a useful catalyst to provide SFL. In the degradation pathway of Fig. 3, SFL may be degraded thermally or even by oxidative agents. SFL is basically thermally stable, however it would be thermally decomposed to sulfur dioxide and polymeric substance at $T=220\text{ }^{\circ}\text{C}$ [34]. Therefore, our results at $T=130\text{ }^{\circ}\text{C}$ in the absence of oxygen may be justified. In the presence of oxygen or oxidizing agents such as chlorates, peroxides and so on,

Table 2 Variation of anions concentration produced by SFL degradation in the presence of O_2 at $T = 130^\circ C$ with gas loading of zero (concentration is based on part per million mass, ppm_w), the uncertainty of concentration obtained from the standard deviation of repetitions

$t/(h)$	Sulfite (ppm _w)	Sulfate (ppm _w)	Thio-sulfate (ppm _w)	Sum ^a (ppm _w)
0	1	1	1	3
22	10	13	1	24
46	14	25	1	40 ± 1.4
118	20 ± 1	38 ± 1	36 ± 1	94 ± 1.7
142	24 ± 1	40 ± 1	23 ± 1	83 ± 1.7
264	68 ± 3	94 ± 4	20 ± 1	182 ± 5.1

^aSum is total sulfur compounds, including sulfite, sulfate and thio-sulfate ions which are based on ppm

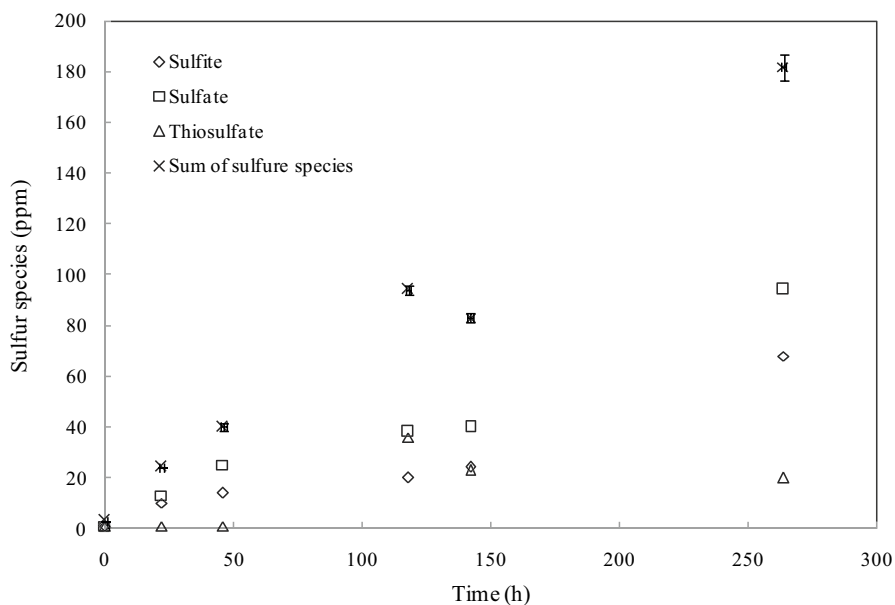


Fig. 2 Comparison of the sulfite, sulfate, thiosulfate ions and total sulfur ion concentration versus time in the presence of oxygen for aqueous 15 wt % SFL

SFL degraded more easily and is followed by generation of SO_2 and in the aqueous media it is prone to hydrolyze to H_2SO_3 or even in presence of more oxidizing agents it transforms into H_2SO_4 . Since all sulfur ions are capable of converting to each other in aqueous media and the presence of oxidizing agents, the formation of other ions (sulfite, sulfate and thiosulfate) can also be justified.

Two other experiments were designed at temperature of the desorption tower ($130^\circ C$) and loaded with carbon dioxide and hydrogen sulfide that one of the experiments was performed without the presence of oxygen (solution A), and another with a primary oxygen partial pressure of 1.0 bar (solution B). The concentrations

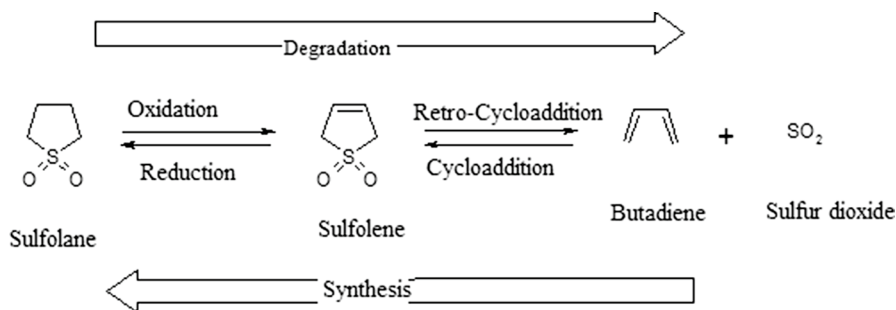


Fig. 3 Degradation and synthesis pathway of SFL

of anions (IC analysis) for solution A are listed in Table 3 and those for solution B are summarized in Table 4 and the sulfur concentration changes (sulfite, sulfate, thiosulfate anions and the total sulfur compounds) in solutions A and B are depicted in Fig. 4a, b, respectively. Due to the presence of SFL, MDEA, PZ and also CO_2 and H_2S in second test, the diversity of undesired degradation products can be observed. The sources of anions sulfite, sulfate and thiosulfate may be from degradation of SFL or the reaction of oxygen with sulfide anions (loaded H_2S) and the sources of other anions like acetate, formate, oxalate and glycolate can be from the oxidative degradation of MDEA and PZ.

Therefore, the study of the concentration changes of these species indicates the progression of oxidative degradation of both amines. As can be seen from Tables 3 and 4 as well as Fig. 4a, b, when the system is loaded by H_2S , it can be rich with sulfide ion and thereby the oxidation of sulfide ions occurs quickly due to the presence of oxidizing agents and then the sulfur ions presented in the system react with ferric and ferrous ions originated from corrosion of equipments and contribute in the precipitation reaction and this leads to the concentration of sulfur ions in the system to reach a constant value. By investigating the concentration of sulfur anions in the two A and B solutions, it can be said that the solution B initially produces more anions due to the higher amount of oxygen. Figure 5 shows molecular SFL concentration changes versus time and it is evident that in both cases the concentrations of SFL are within their uncertainty values showing that SFL is not degraded because the oxidizing agents in system react with more convenient compounds such as sulfide ions, so SFL is not degraded. According to the fact that in gas refineries the presence of hydrogen sulfide in desorption tower is in considerable values, the presence of any type of oxidizing agent causes the formation of sulfur anions and thereby corrosion increases sharply. It means that the SFL degradation in operational condition in sweetening units is not the significant reason for corrosion. The question that may arise from this result is why corrosion increased with SFL concentration? SFL is likely to increase O_2 absorption capacity of solvents and it makes solvent a context in which O_2 more easily degrades other species such as alkanolamine. The measure of oxygen solubility is not the aim of present work, however for nearer prospect to get a sense for increasing corrosion, degradation of MDEA and PZ have been accounted in this work. The concentration variation of amine solvents

Table 3 Variation of different anions concentration produced with solvent degradation at 130 °C loaded with H₂S and CO₂ in the absence of air (A solution), concentration is based on part per million mass, ppm_w and the uncertainty of concentration obtained from the standard deviation of repetitions

<i>t</i> (h)	Acetate (ppm _w)	Formate (ppm _w)	Chloride (ppm _w)	Nitrate (ppm _w)	Nitrite (ppm _w)	Oxalate (ppm _w)	Sulfite (ppm _w)	Sulfate (ppm _w)	Phosphate (ppm _w)	Thio- cyanate (ppm _w)	Thiosulfate (ppm _w)	Sum ^a (ppm _w)
0	<1	<1	2	<1	<1	<1	<1	1	<1	<1	<1	
1	1	1	62	1	1	22	531	134	1	33	439	1104 ± 21
5	1	38 ± 1	62	1	1	22 ± 1	347 ± 14	87 ± 3	1	69	386 ± 15	820 ± 21
30.25	51 ± 2	168 ± 6	62	1	39 ± 1	22 ± 1	191 ± 8	75 ± 3	1	246 ± 10	127 ± 5	393
98	377 ± 15	345 ± 13	62	1	45	22 ± 1	245 ± 10	67 ± 3	1	82 ± 3	138 ± 5	450 ± 11.6
192	601 ± 24	486 ± 19	84	1	1	21 ± 0.8	161 ± 6	49	157 ± 6	1	141 ± 5	351 ± 8.1
265	852 ± 34	588 ± 23	79	1	39	22 ± 1	160 ± 6	50 ± 2	155 ± 6	1	168 ± 6	378
360	1209 ± 48	700 ± 28	72	1	41	26 ± 1	147 ± 5	87 ± 3	1	1	72 ± 2	306 ± 6.2
433	1507 ± 60	753 ± 30	73	1	1	27 ± 1	164 ± 6	85 ± 3	1	1	88 ± 3	337 ± 7.2
531	1616 ± 65	611 ± 24	66	1	40	35 ± 1	174 ± 7	77 ± 3	1	1	101 ± 4	352 ± 8.2

^aSum is the total sulfite, sulfate and thiosulfate ions which are based on ppm_w

Table 4 Variation of different anions concentration produced with solvent degradation at 130 °C (B solution), concentration is based on part per million mass, ppm_w, and the uncertainty of concentration obtained from the standard deviation of repetitions

<i>t</i> (h)	Acetate (ppm _w)	Formate (ppm _w)	Chloride (ppm _w)	Nitrate (ppm _w)	Nitrite (ppm _w)	Oxalate (ppm _w)	Sulfite (ppm _w)	Sulfate (ppm _w)	Phosphate (ppm _w)	Thiocyanate (ppm _w)	Thiosulfate (ppm _w)	Sum ^a (ppm _w)
0	< 1	< 1				< 1	< 1	< 1	< 1	< 1	< 1	
1	1	1	62	1	1	22	531	134	1	33	439	1104 ± 23.5
5	1	137 ± 5	62	1	1	22	334 ± 13	217 ± 8	1	86 ± 3	743 ± 29	1294 ± 32.4
30	1946 ± 77	977 ± 39	62	1	48	34 ± 1	246 ± 10	191 ± 8	1	47	253 ± 10	690 ± 16.2
98	4101 ± 164	1272 ± 51	62	1	46	34 ± 1	203 ± 8	196 ± 8	1	31	230 ± 9	629 ± 14.5
192	4436 ± 177	1339 ± 53	62	1	46	31 ± 1	178 ± 7	193 ± 8	1	30	127 ± 5	498 ± 11
265	4823 ± 192	1365 ± 54	62	1	41	32 ± 1	152 ± 6	195 ± 7	1	1	151 ± 6	498 ± 11
360	4645 ± 185	1412 ± 56	72	1	38	36 ± 1	116 ± 4	196 ± 7	1	1	108 ± 4	420 ± 9
433	4779 ± 191	1376 ± 55	73	1	1	38 ± 1	97 ± 3	197 ± 7	1	1	164 ± 6	458 ± 9.7
531	4825 ± 193	1155 ± 60	72	1	40	45 ± 1	143 ± 5	200 ± 8	1	1	106 ± 4	449 ± 10.2

^aSum is total sulfite, sulfate and thiosulfate ions which are declared with ppm_w

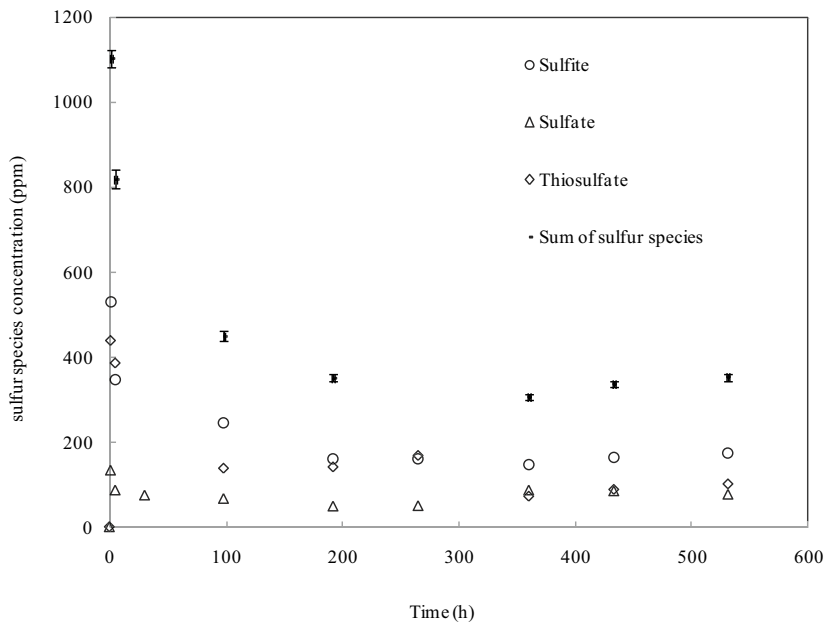
(MDEA and PZ) and also DEA and MMEA, which are both the products of the oxidative degradation of MDEA and PZ is measured by gas chromatography and with the SFL concentration, are summarized in Tables 5 and 6. The results listed in Tables 5 and 6 show that during the given time, MDEA and PZ were degraded to about 8.5 and 46 wt % in solution A, respectively. These values were 15.1 % and 53.8 % for MDEA and PZ in solution B, respectively. Comparison of MDEA and PZ degradation in the two above solutions shows that the effect of oxygen in the solution accelerates both thermal degradation of carbamate polymerization and oxidative degradation of MDEA and PZ, but as already mentioned, projection of variation concentration of acetate and formate can give us information about the oxidative degradation of these two amines. Figure 6 shows concentration changes of acetate and formate anions. By investigating the concentration changes of acetate and formate in both solutions A and B, it is found that the concentration of acetate ion in solution A increase from zero at the beginning of the test and reached 1600 ppm and the concentration of formate ion reached 750 ppm and for solution B, the concentration of acetate ion has reached from zero to 4800 ppm and the concentration of formate ion reached 1155 ppm which indicates an increase in the oxidative degradation of amines (MDEA and PZ) in solution B. It should be noted that the main product of the carbamate polymerization degradation which is in the form of various derivatives of oxazolidone has not been investigated in this work. As a secondary product, the formation of DEA is possible by transferring a methyl group from MDEA and also MMEA by transferring a hydroxy ethyl group from MDEA or through a radical oxidation mechanism [35] and considering that DEA and MMEA can participate in the carbamate polymerization reactions, hydroxyl ethyl oxazolidone product has also been observed in the oxidative degradation of MDEA which is out of the scope of this study.

Fig. 4 (a) Comparison of sulfur ions species (sulfite, sulfate and thiosulfate) concentration changes with time in solution A. (b) Comparison of sulfur ions species (sulfite, sulfate and thiosulfate) concentration changes with time in solution B

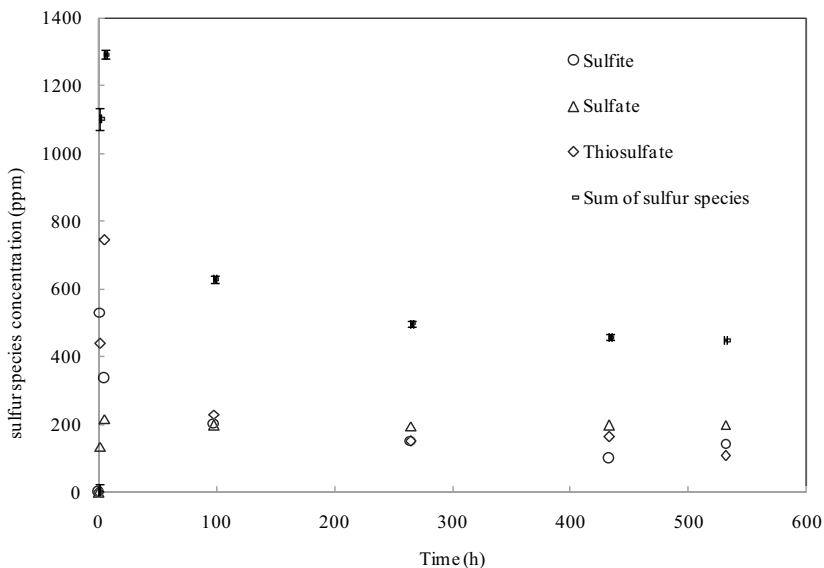
4 Conclusion

Rostami and Tavan [6] experimentally inspected the industrial sour gas stream of the Ilam gas-treating unit by substituting hybrid solvent for the aqueous one. They showed that foaming and corrosion were increased with addition of SFL in aqueous MDEA + PZ solution. Degradation of SFL and increasing of O_2 solubility by SFL addition may be regarded as two reasons of this result. In this work, we evaluated the degradation of hybrid solvent containing SFL in the presence of oxygen. For this purpose, two experiments were carried out: (1) degradation of SFL in 15 wt % of aqueous SFL solution in the presence and absence of O_2 at 130 °C; (2) degradation of gas-loaded hybrid solvent containing SFL, MDEA, PZ, H_2S and CO_2 in the presence and absence of O_2 at 130 °C to make a real condition. The following results were obtained from the experiments. At the operational condition studied, SFL is thermally stable, however in presence of 1 bar O_2 at 130 °C during 3 weeks is degraded to sulfite, sulfate and thiosulfate anions. The amount of SFL degradation under the mentioned condition is in order of 10^{-6} (part per million mass, ppm_w). In the presence of sulfide ions originating from H_2S in solution, oxygen immediately reacts with them. In this case, SFL is not degraded, therefore the presence or absence of SFL is an irrelevant issue. By regarding the results of second test, one can find that the second scenario of the cause of increasing of solvent corrosion by adding of SFL gets highlighted. It means that adding SFL makes it an implicated context to absorb more O_2 physically and thereby the presence of O_2 greatly enhances the degradation of other species other than SFL in the mixed solvent (namely MDEA and PZ).

To prevent oxidative degradation of hybrid solvents which contain SFL, some corrections should be done in refinery equipments to prevent entrance of air in various sectors, or by adding an appropriate inhibitor in solvent formulation; O_2 gets removed or scavenged during gas processing or even solvents containing SFL are stored or employed under a nitrogen blanket to be out of contact with oxygen or strong oxidizing agents. Investigations on O_2 solubility in hybrid solvents, choosing a proper inhibitor and nitrogen blanketing will be studied in future.



(a) Comparison of sulfur ions species (sulfite, sulfate and thiosulfate) concentration changes with time in solution A.



(b) Comparison of sulfur ions species (sulfite, sulfate and thiosulfate) concentration changes with time in solution B.

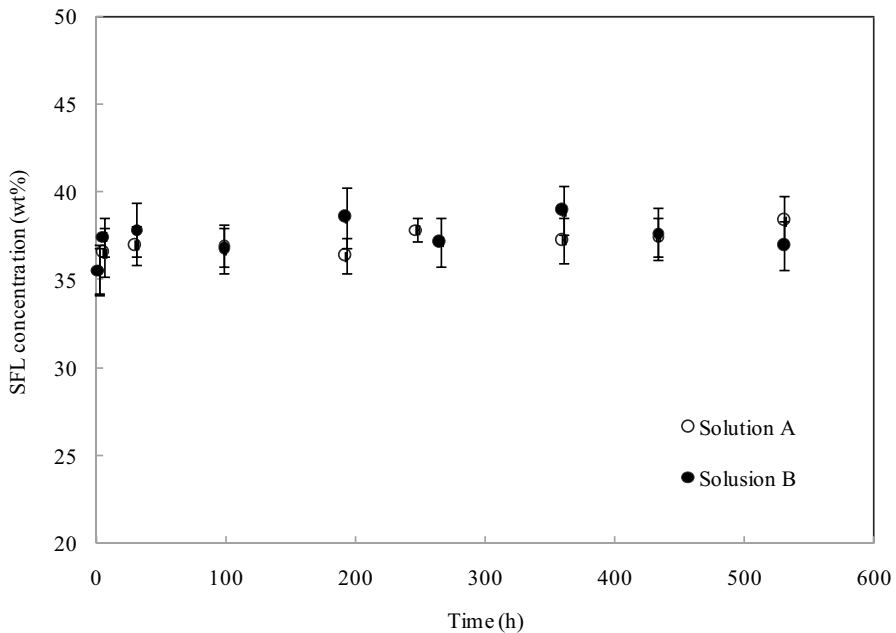


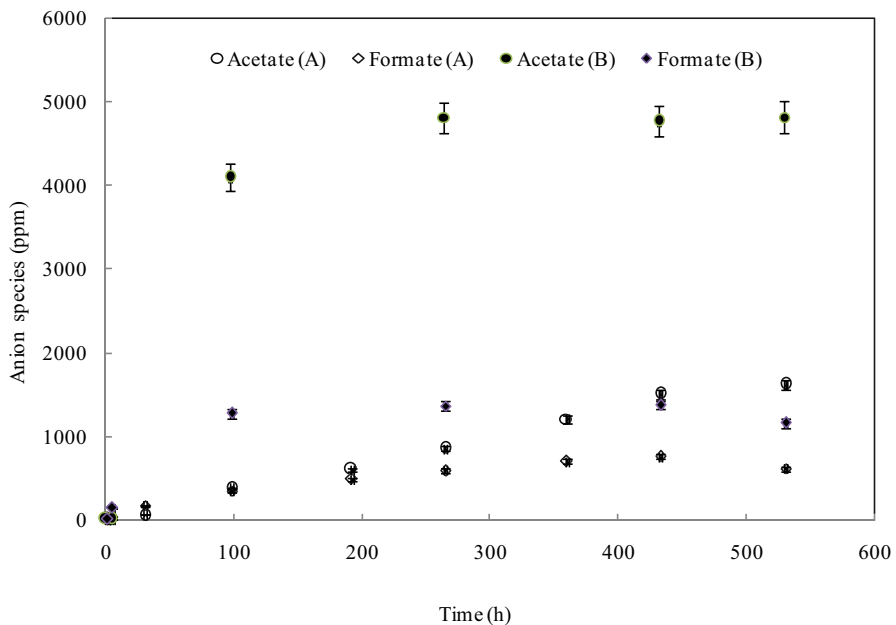
Fig. 5 Comparison of SFL concentration changes versus time for solutions A and B

Table 5 Variation of solvent components concentration due to degradation (based on mass percent, wt %) at 130 °C loaded with H₂S and CO₂ in the absence of oxygen (A solution)

	<i>t</i> (h)	H ₂ O (wt %)	PZ (wt %)	MDEA (wt %)	SFL (wt %)	MMEA (wt %)	DEA (wt %)
	0		1.3	25.6	35.6	0	0
A0	1	37.2	1.3 ± 0.04	25.6 ± 1.0	35.6 ± 1.4	0	0
A1	5	37.2	1 ± 0.02	25.5 ± 0.7	36.6 ± 1.4	0.05	0
A2	30	36	1.1 ± 0.03	25.4 ± 0.7	37 ± 1.1	0.18	0.08
A3	98	36.7	1.1 ± 0.02	24.6 ± 0.9	36.9 ± 1.1	0.26	0.2
A4	192	36.6	0.9 ± 0.03	24.9 ± 0.9	36.4 ± 1.0	0.3	0.45
A5	247	36.1	1 ± 0.03	24 ± 0.7	37.9 ± 0.7	0.33	0.5
A6	360	35.6	0.9 ± 0.03	24.3 ± 0.9	37.3 ± 1.3	0.35	0.6
A7	433	35.4	0.9 ± 0.04	24 ± 0.9	37.5 ± 1.1	0.4	0.6
A8	531	35	0.7 ± 0.02	23.4 ± 0.7	38.4 ± 1.4	0.4	0.6
deg %			42.2	8.6	~ 0		

Table 6 Concentration changes of the solvent components (based on mass percent, wt %) at 130 °C loaded with H₂S and CO₂ in the presence of oxygen (B solution)

	<i>t</i> (h)	H ₂ O (wt %)	PZ (wt %)	MDEA (wt %)	SFL (wt %)	MMEA (wt %)	DEA (wt %)
	0		1.3	25.6	35.6		
B0	1	37.2	1.3 ± 0.04	25.6 ± 0.7	35.6 ± 1.3	0	0
B1	5	37	1.0 ± 0.03	24.3 ± 0.9	37.5 ± 1.1	0	0
B2	30.25	36	0.8 ± 0.03	24.1 ± 0.9	37.9 ± 1.5	0.4	0.2
B3	98	35.9	1.0 ± 0.03	24.5 ± 0.7	36.8 ± 1.4	0.6	0.4
B4	192	35.9	0.9 ± 0.03	23.1 ± 0.6	38.2 ± 1.7	0.5	0.45
B5	265	36.3	0.9 ± 0.02	23.3 ± 0.6	37.2 ± 1.4	0.6	0.6
B6	360	36.1	0.7 ± 0.03	22.1 ± 0.6	38.0 ± 1.4	0.5	0.4
B7	433	36.1	0.8 ± 0.03	22.4 ± 0.8	37.7 ± 1.5	0.64	0.6
B8	531	37.6	0.6 ± 0.02	21.7 ± 0.8	37 ± 1.4	0.5	0.5
deg %			53.8	15.2	~ 0		

**Fig. 6** Comparison of acetate (circle) and formate (diamond) ion concentration changes curve versus time in solution A and B (fill markers are from solution B and no fill markers are from solution A)

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