STM JOURNALS

Journal of
Petroleum Engineering & Technology

ISSN: 2231-1785 (Online)
ISSN: 2321-5178 (Print)
Volume 15, Issue 1, 2025
January–April
DOI (Journal): 10.37591/JoPET

https://journals.stmjournals.com/jopet

Research JoPET

Novel Amino Silanes for Inhibition and Dissolution of Aldol Polymer for Caustic Tower in Cracker Plant

Hiren M. Bhajiwala[1], Harshad Patil[2], Virendrakumar Gupta[3,*]

Abstract

Aldol polymer fouling in petrochemical plant is an undesirable process, which needs to be removed for increasing the efficiency of downstream process. In this paper, inhibition and dissolution efficiency of the aminopropyl trimethoxy silane (APTMS), aminopropyl triethoxy silane (APTES), sodium salt of aminopropyl trimethoxy silane (SS-APTMS), sodium salt of aminopropyl triethoxy silane (SS-APTES) were studied at different molar ratio of vinyl acetate (VA):amino alkoxy silane (antipolymerant). The sodium salt of 6-aminohexanoic acid (SS-AHA) and ethanolamine (EA) were used as reference for comparison. The efficiency of antipolymerant for inhibition and dissolution was measured as percentage transmission (% T) by UV spectrophotometry. Solium salt of amino alkoxy silane showed good efficiency for inhibition and dissolution process. Furthermore, the presence of alkoxy group with amino group facilitates inhibition as well as dissolution of aldol polymer in alkaline media, while compounds with amino group acts as inhibitor for aldol condensation only.

Keywords: Aldol condensation, fouling, inhibition, dissolution, amino alkoxy silane, % transmission

INTRODUCTION

Ethylene, propylene, butylene, and butadiene are key petrochemical raw ingredients used in the manufacturing of polymers and elastomers [1, 2]. These basic ingredients are more often generated by breaking heavier hydrocarbons. In general, the cracking process known as pyrolysis occurs when bigger alkane molecules break down into smaller alkanes and an alkene at extremely high temperatures [3]. In this process, acidic hydrogen sulfide is produced by the reaction of hydrogen and sulfur, whereas carbon dioxide is produced via water-gas reactions and reforming, as well as the primary olefin products. Aside from the main olefin products, a small number of carbonyl components such as aldehydes and ketones, as well as a variety of aliphatic and aromatic components, are produced [4–6]. In the commercial plant, the combination of fractured gas stream must pass through a basic scrubber to remove the acidic component, which is hazardous to the downstream process (Figure 1).

***Author for Correspondence**
Virendrakumar Gupta
E-mail: virendrakumar.gupta@ril.com

[1]Deputy General Manager, Polymer Synthesis & Catalysis, Reliance Research and Development Centre, Reliance Industries Limited, Navi Mumbai, Maharashtra, India
[2]Senior General Manager, Polymer Synthesis & Catalysis, Reliance Research and Development Centre, Reliance Industries Limited, Navi Mumbai, Maharashtra, India
[3]Senior Vice President and Head, Polymer Synthesis & Catalysis, Reliance Research and Development Centre, Reliance Industries Limited, Navi Mumbai, Maharashtra, India

Received Date: January 06, 2025
Accepted Date: January 11, 2025
Published Date: January 23, 2025

Citation: Hiren M. Bhajiwala, Harshad Patil, Virendrakumar Gupta. Novel Amino Silanes for Inhibition and Dissolution of Aldol Polymer for Caustic Tower in Cracker Plant. Journal of Petroleum Engineering & Technology. 2025; 15(1): 35–48p.

Sodium hydroxide and potassium hydroxide are widely used in caustic towers to eliminate acidic components from crack gas. However, in rare cases, very basic ethanolamine, diethanolamine, and butyl amine were described as crack gas cleaning materials [7, 8]. Nonetheless, the basic state of scrubber material catalyzed the aldehyde and ketone contained in crack gas, which then underwent aldol condensation to generate red oil. Furthermore, red oil polymerizes to generate larger molecular weight, insoluble aldol polymers [4–6]. The insoluble aldol polymer tends to be deposited in caustic tower trays, reducing process efficiency and, in certain cases,

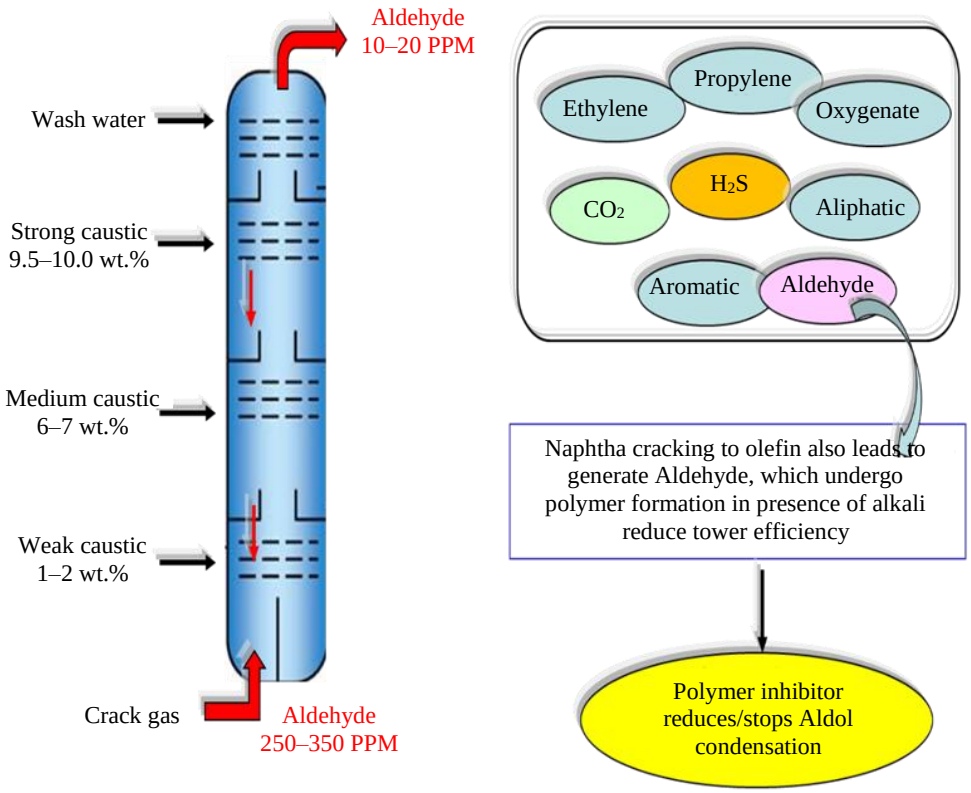


Figure 1. Aldol polymer formation in caustic tower of the cracker plant.

causing the cracking operation to be shut down. Electron donating aliphatic and aromatic chemicals are commonly utilized as inhibitors of aldol polymer formation, as documented in various studies [5]. Inhibitors react with aldehyde to form a compound that does not polymerize further; also, inhibitors aid in the removal of fouling from the scrubber's inner workings. Inhibitors such as amino phenol, amino benzoic acid and its salts [5], urea-keto urea [7], ethylenediamine [8], borohydride [9], hydroxylamine and its salts [10], hydrazine and its derivatives [11], carbohydrazine and its derivatives [4], and acetoacetate esters compounds [12] have been reported in various literature to inhibit aldol polymer formation. All of the above-mentioned chemicals primarily function as inhibitors of the aldol process; once polymers are formed, these compounds become useless. Subramaniyam et al. [13, 14] reported an amino acid based on lactam and an inorganic salt of dithionite as an antipolymerant, which not only inhibits aldol reaction but also dissolves higher molecular weight polymer fouling generated in caustic tower, resulting in an advantage over all conventional amino-based compounds.

There are very few quantitative studies available in the open literature on the suppression of the aldol process. We thoroughly explored the effect of antipolymerant with various functional groups, as well as the influence of catalyst concentration, reaction duration, temperature, and aldehyde to inhibitor molar ratio.

EXPERIMENTAL

Materials

Vinyl acetate (VA), aminopropyl trimethoxy silane (APTMS, 99%), aminopropyl triethoxy silane (APTES, 98.5%), sodium hydroxide (NaOH) of AR grade were obtained from SD Fine Chemical Product, India. Sodium salt of aminopropyl trimethoxy silane (SS-APTMS), and sodium salt aminopropyl triethoxy silane (SS-APTES) were synthesized at lab scale and used as antipolymerant. Sodium salt of 6-aminohexanoic acid synthesized in the lab and used as a reference chemical. Ethanol amine (EA, 99.5%) obtained from Labort Fine Chemical, Surat, India, was also employed as a reference compound.

Aldol Reaction Inhibition Performance of Antipolymerant

The efficiency of an antipolymerant in stopping the aldol process was investigated using amino alkoxy silane. The chemical was combined with 40 mL of a 2.5 M aqueous sodium hydroxide solution in a flat-bottomed flask and swirled on a heated plate at 350 rpm. Vinyl acetate was added to the mixture while stirring at a constant rate. The reaction's progress was tracked by measuring the solution's absorbance at 800 nm with a UV spectrophotometer (PE Lambda35) at predetermined time intervals to determine inhibition effectiveness [7]. A control experiment was conducted under the same conditions, but without the antipolymerant and using previously known amine derivatives. Furthermore, the molar ratio of vinyl acetate to amino alkoxy silane (8:1, 4:1, and 1:1) as well as the impact of temperature (40°C and 55°C) were examined (Scheme 1).

Aldol Reaction Dissolution Performance of Antipolymerant

Vinyl acetate (0.021 mol) was mixed with 40 mL (2.5 M) caustic solution in a 100-mL conical flask while stirring. The color of the solution turns to hazy yellow after a few minutes due to aldol condensation of acetaldehyde produced by VA hydrolysis under alkaline conditions. After 15 minutes, a yellow precipitate of aldol polymer appeared. To test amino acid dissolving efficiency, a varied VA:antipolymerant ratio was added to this solution, and the solution's transmittance was measured at 800 nm by a UV spectrophotometer after 30 minutes of exposure. To compare the performance of the described amine derivatives, the dissolution of aldol condensation polymer was investigated (Scheme 1).

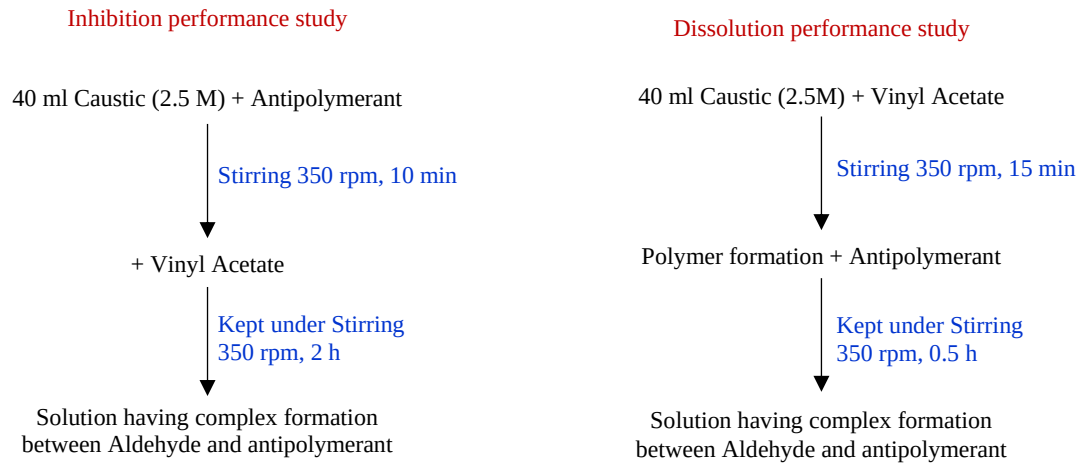
Characterization Studies

Nuclear Magnetic Resonance Study

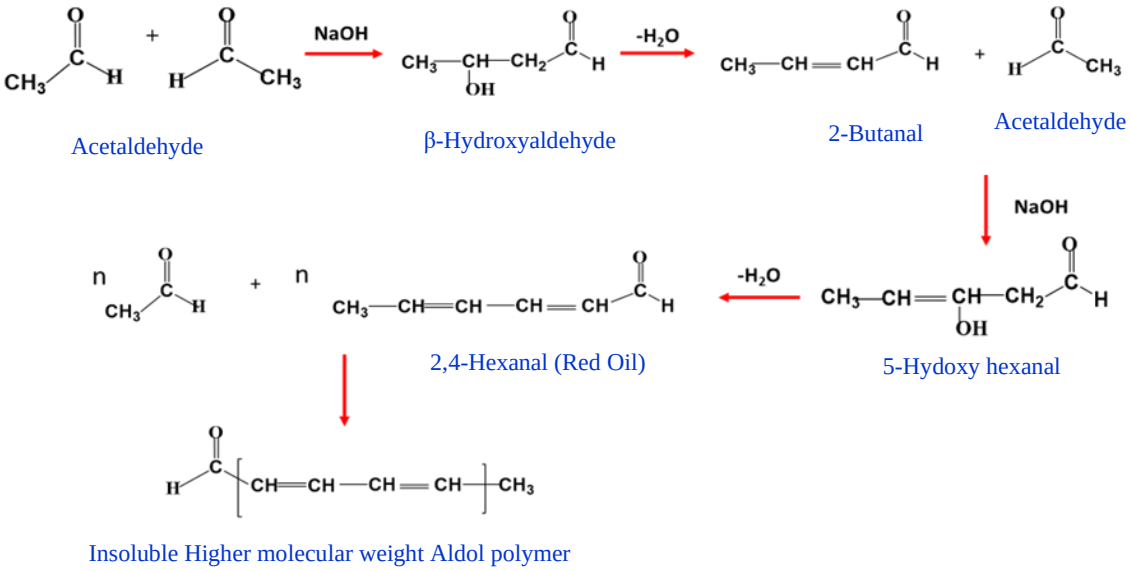
The proton nuclear magnetic resonance (NMR) spectrum was measured with a Brucker FT NMR Advance 400 spectrometer in D2O at 400 MHz frequency. A delay time of 10 s was given for recording 1H NMR spectra. The signal intensities of the spectra peak were measured from the integrated areas calculated with electronic integrator. NMR measurements were made on 10% (w/v) polymer solutions. The proton replacement was calculated based on proton concentration of -OCH_3 group.

RESULTS AND DISCUSSION

Red oil formation is more common phenomenon observed in olefin production plant due to aldol condensation of aldehyde molecule in presence of base as catalyst, which is further converting to higher molecular weight insoluble polymer. The mechanism of red oil formation is depicted in Scheme 2. In this reaction two molecule of aldehyde reacts in basic media, forms β-hydroxy aldehydes via reactive enolate. Furthermore, 2-butanal having double bond generates due to removal of water from β-hydroxy aldehydes. Further similar reaction undergoes in presence of another aldehyde molecule with α-hydrogen of 2-butanal and generates conjugated double bond 2,4-hexanal (red oil). The red oil is generally soluble in caustic but insoluble in water [15].



Scheme 1. Inhibition and dissolution methodology for performance study of antipolymerant.



Scheme 2. Aldol polymer formation reaction mechanism.

A total of 0.03 moles of APTMS/APTES and 0.12 moles of caustic soda were stirred and heated to 40°C for 1 hour. The water content in the reaction mixture was removed by evaporation to get a dry salt and used for ^{1}H NMR. The change in concentration of proton in pure APTMS/APTES and sodium salt of APTMS/APTES was investigated through NMR to ascertain the conversion of APTMS/APTES to SS-APTMS and SS-APTES. ^{1}H NMR shown in Figure 2 of pure APTMS having nine protons of $–OCH_3$ group attached to Si shows signals between 3.0 and 3.4 ppm while Figure 3 indicates replacement of nearly four protons indicating that synthesized salt is predominantly monosubstituted sodium salt. In Figure 4 APTES having nine protons of $–CH_3$ group shows signals between 0.80 and 0.87 ppm and six protons of $–OCH_2$ group show two signals at 3.4 and 3.2 ppm. Figure 5 indicates that there was a replacement of approximately four protons from the $-CH_3$ groups and replacement of approximately three protons from $–OCH_2$ groups indicating the formation of predominantly monosubstituted sodium salt (Table 1). Proton NMR study indicated that four and seven protons are replaced in APTMS and APTES, which indicated formation predominantly of mono substituted salt of APTMS and monosubstituted salt of APTES.

The inhibition performance of APTMS / APTES and SS-APTMS / SS-APTES investigated for aldol reaction and compared with reference SS-AHA and EA antipolymerant (Scheme 3). All the experiments were conducted in 40 mL of 10% caustic solution followed by addition of antipolymerant and vinyl acetate. The experiments were conducted at 8, 4 and 1 VA:antipolymerant ratio and two different temperature 40°C and 55°C. Furthermore, this reaction was catalyzed by caustic, which convert vinyl acetate to acetaldehyde via hydrolysis and further polymerized to formed insoluble solid. Efficiency of the inhibition reaction was measured by percentage transmission (%T) on a UV spectrophotometer at 800 nm after 2 hours. Percentage transmission (%T) was a direct reflection of efficiency of antipolymerant for prevention of aldol condensation reaction. higher %T reflect better inhibition of aldol reaction, whereas lower %T indicates less effectiveness for inhibition of aldol reaction.

Table 1. Proton NMR study of synthesized sodium salt of APTMS and sodium salt of APTES.

S.N.	Compound	No. of protons replaced	No. of alkyl groups of alkoxy silane replaced by sodium	Type of sodium salt formed from alkoxy silane
1	APTMS	4	1	Mono substituted
2	APTES	7	1	Mono substituted

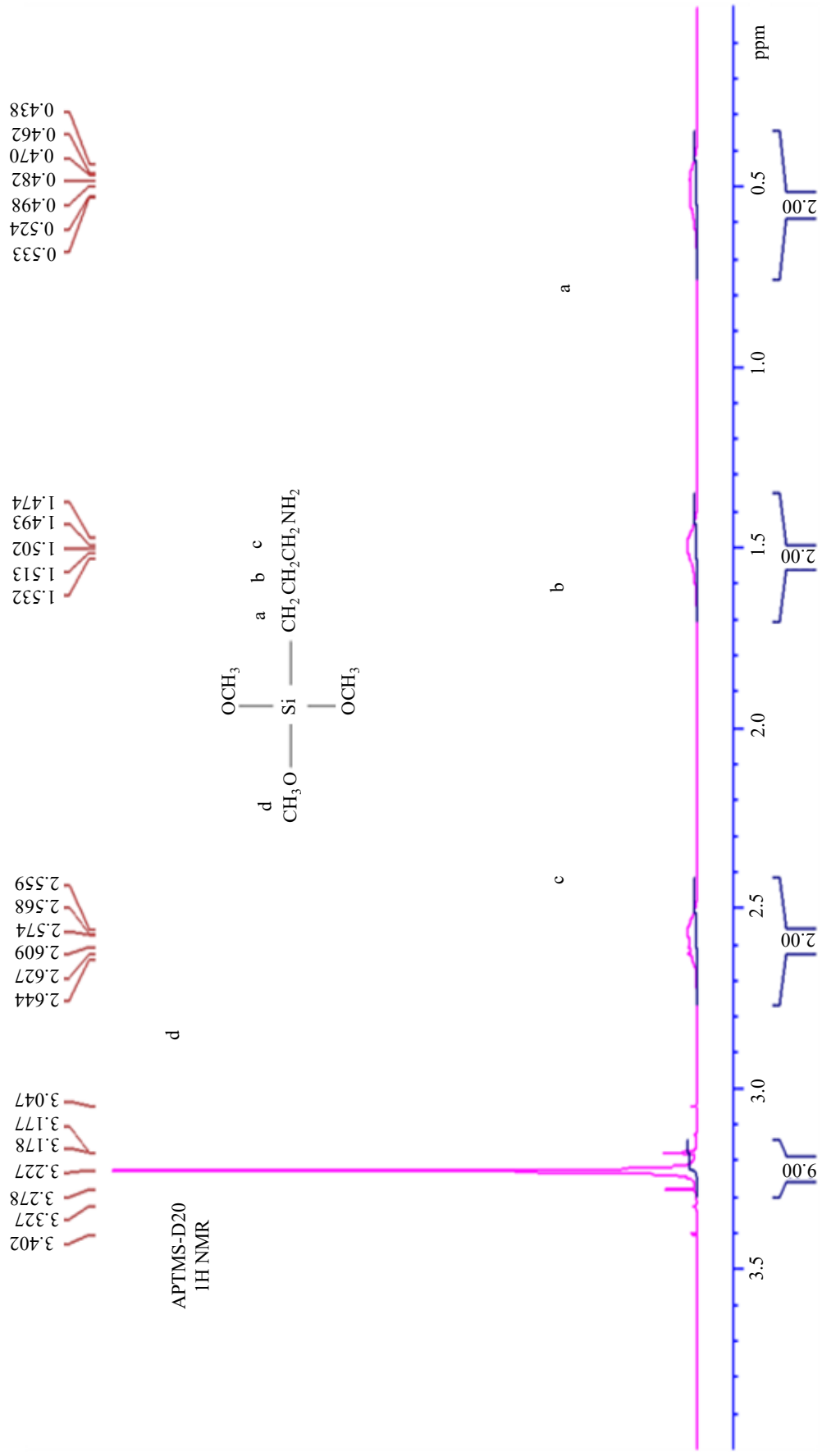


Figure 2. ^{1}H NMR spectrum of pure APTMS.

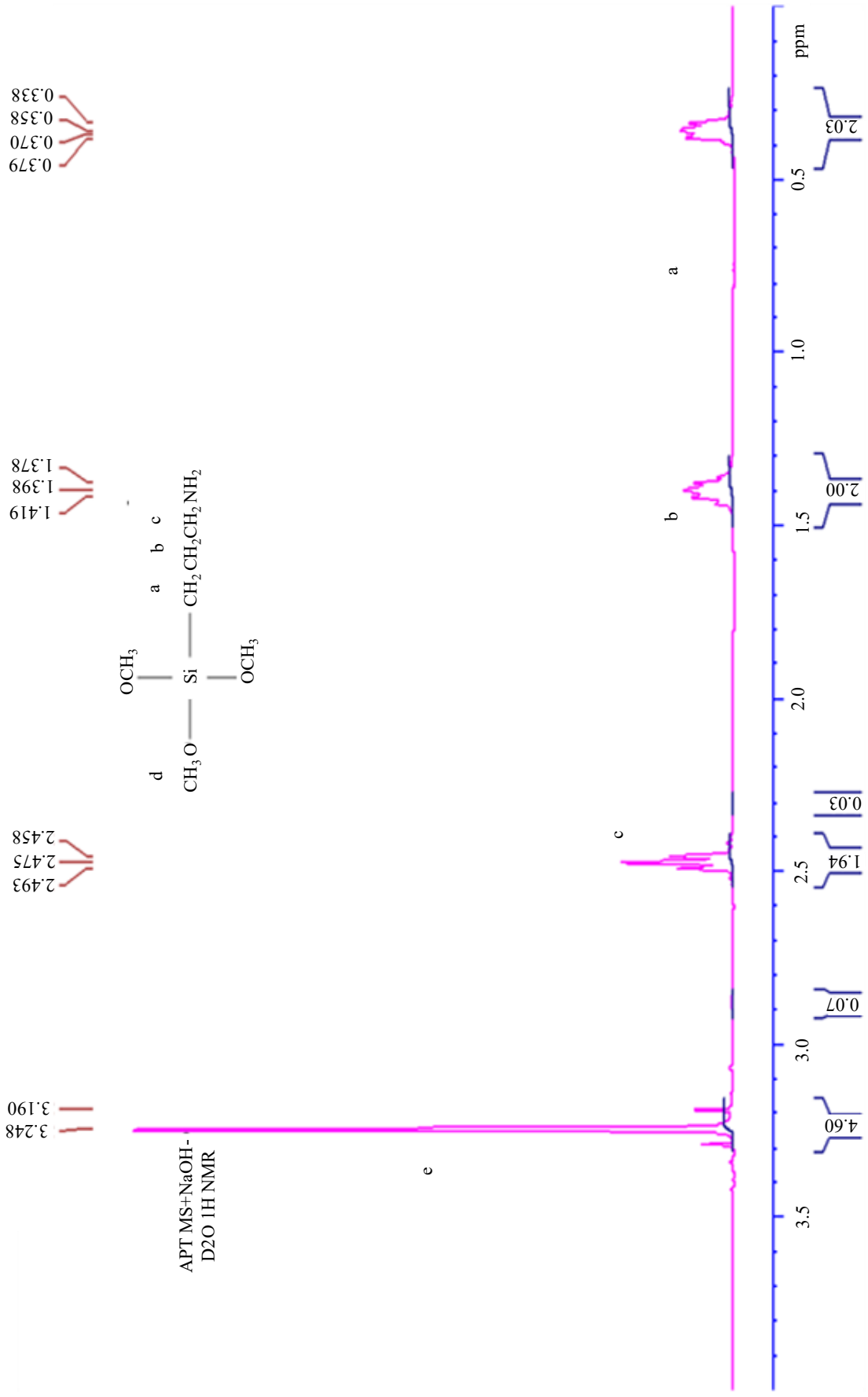


Figure 3. ^{1}H NMR spectrum of APTMS after reaction with NaOH.

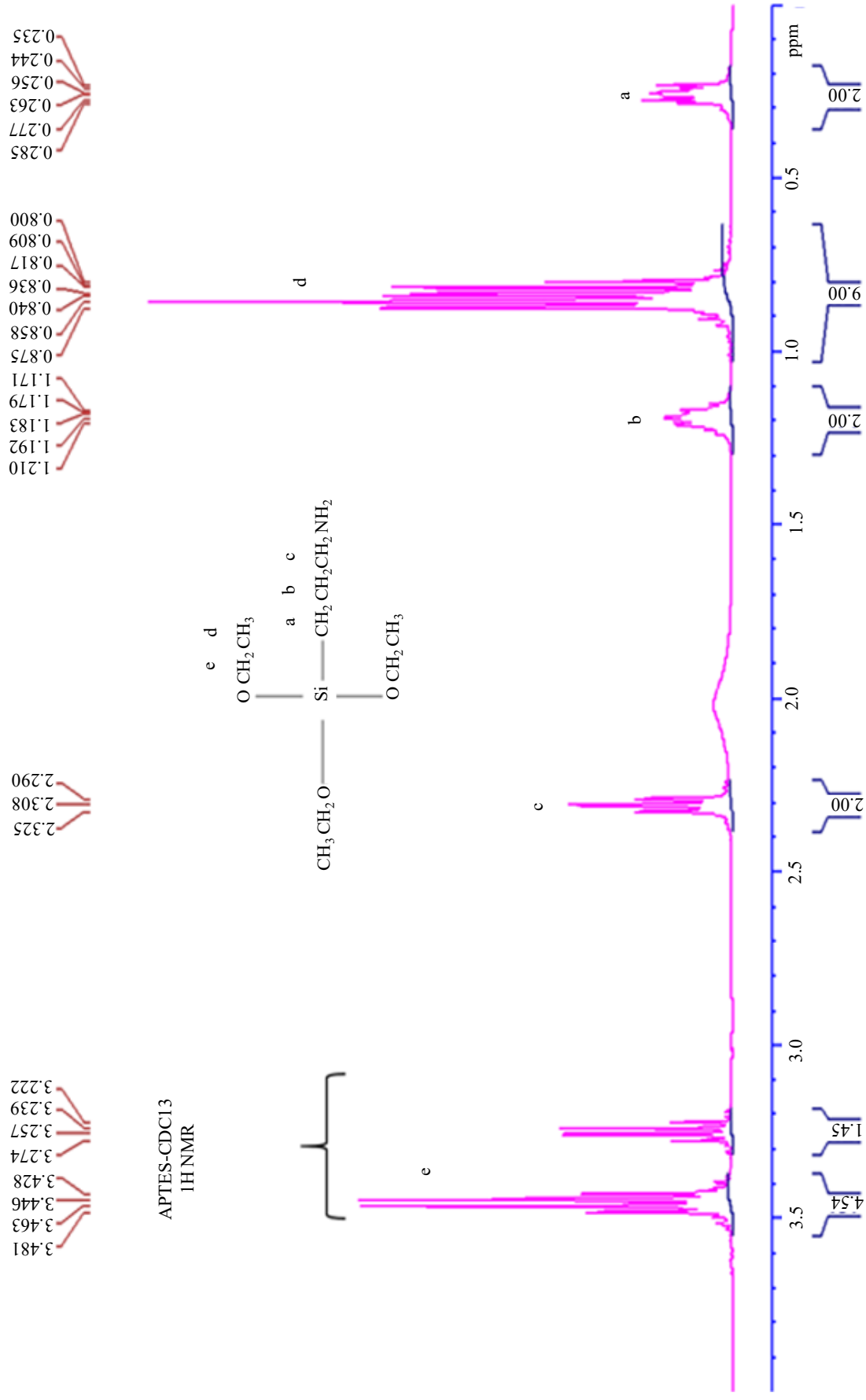


Figure 4. ^{1}H NMR spectrum of pure APTES.

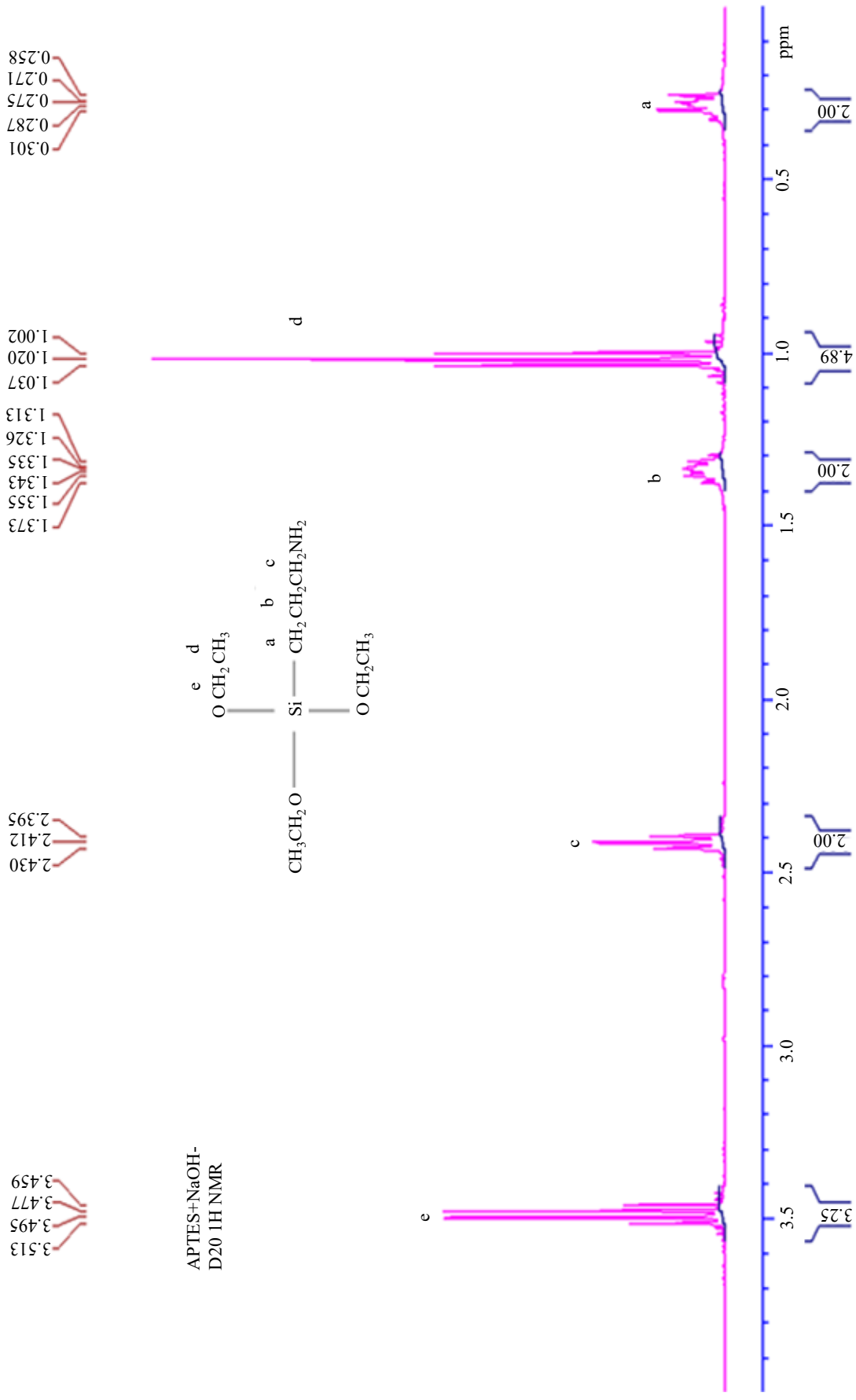
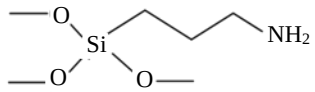
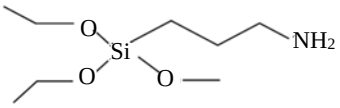


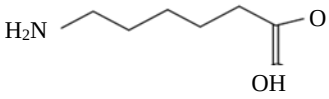
Figure 5. ^{1}H NMR spectrum of APTES after reaction with NaOH.



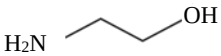
Aminopropyl trimethoxy silane (APTMS)



Aminopropyl trimethoxy silane (APTES)



6-Aminohexanoic acid (AHA)



Ethanolamine

Scheme 3. Antipolymerants used for inhibition and dissolution of aldol condensation.

The inhibition performance of APTMS/APTES and SS-APTMS/SS-APTES at 40°C showed 96% to 99% T at all 8, 4 and 1 VA:antipolymerant ratio, which is almost slimier to respective VA:antipolymerant ratio of reference SS-AHA. Whereas EA showed slightly lower % T 89, 91 and 94 at 8, 4 and 1 VA:antipolymerant, respectively. Higher %T of APTMS/APTES and SS-APTMS/SS-APTES and SS-AHA exhibited, batter control or inhibition of aldol condensation reaction (Table 2), this is due to reaction of electron donating -NH_2 group of antipolymerant with carbonyl group of acetaldehydes, formed intermediate carbinolamine, which further undergoes loss of water molecule to produce imine [16, 17]. These results are in good agreement with work reported previoully [18, 19].

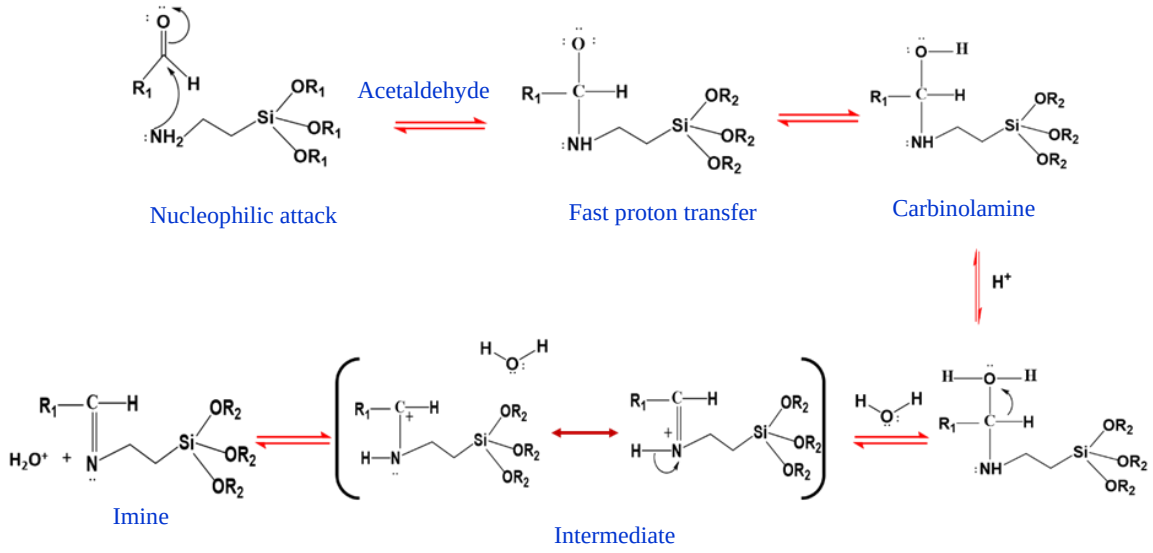
Moreover, slightly lower %T of EA found due to presence of -OH group with -NH_2 in the structure (Table 2). Imine production begins with a nucleophilic assault of the main amine's nitrogen lone pair on the electrophilic carbon of the aldehyde or ketone's carbonyl group. The first step results in a tetrahedral intermediate where the carbonyl carbon undergoes sp^2 to sp^3 hybridization. Following this, a proton transfer occurs, stabilizing the intermediate by turning the carbonyl oxygen into a hydroxyl group (-OH) and protonating the amine nitrogen. This produces a carbinolamine intermediate, which is required for the following step.

The carbinolamine is dehydrated, a process in which the hydroxyl group is protonated to become a better leaving group, resulting in the removal of water. This step restores the carbon atoms sp^2 hybridization and forms a double bond between the carbon and nitrogen. The consequence is the creation of an imine (R-C=NR'), which is the reaction's ultimate product. This reaction is reversible, and the equilibrium between the carbinolamine intermediate and the imine favors imine synthesis under dehydrating conditions or by eliminating water from the solution. Due to imine formation, it inhibited the reaction; hence the %T was found to be higher as antipolymerant amount increases (Scheme 4).

Furthermore, similar experiments at 55°C temperature found <1 to 2% T at higher 8 VA:antipolymerant ratio for APTMS/APTES and SS-APTMS/SS-APTES. Whereas significantly higher %T in case of SS-AHA indicates that at higher concentration long chain amino acid type compound capable to make better bond formation compared to functional ground having alkoxy and amino group. However, at lower 4 and 1 VA:antipolymerant ratio APTMS/APTES and SS-APTMS/SS-APTES showed 89% to 98% T, which is significantly higher compared to 8 VA:antipolymerant ratio. These results revealed that enough amount of antipolymerant required in case of amino alkoxy silane type antipolymerant. Overall inhibition performance sequence at 40°C and 55°C for 8, 4 and 1 VA:antipolymerant ratio were found to be SS-AHA > SS-APTES >SS-APTMS > APTES > SS-APTMS > EA. The appearance of solution after 2 hours without antipolymerant and with antipolymerant is shown Figure 6.

Table 2. Inhibition performance study of antipolymerant for aldol condensation reaction at different vinyl acetate (VA):antipolymerant ratios.

No	Compound	Mole ratio of VA to additives	% T at 800 nm on UV (% T ± 2)	% T at 800 nm on UV (% T ± 2)
			After 2 hours at 40°C	*After 2 hours at 55°C*
1	APTMS	8	95	<1
2		4	96	92
3		1	99	98
4	APTES	8	96	<1
5		4	99	89
6		1	98	98
7	SS-APTMS	8	96	<1
8		4	97	92
9		1	99	98
10	SS-APTES	8	97	2
11		4	99	93
12		1	99	98
13	SS-AHA	8	95	81
14		4	99	99
15		1	99	99
16	EA	8	89	<0.1
17		4	91	40
18		1	94	90



where – R_1= CH_3
R_2= -CH_3 or -CH_2CH_3

Scheme 4. Proposed mechanism of inhibition of aldol condensation reaction while using of antipolymerant.

Most of the primary amino, amino acids, amnio alkoxy, amino alkoxy silane and amino alcohol has good inhibition properties towards aldol condensation, however very few compounds are known for dissolution of aldol polymer such as long chain amino acid [13]. In this study, we investigated APTMS/APTES and SS-APTMS/SS-APTES for dissolution of aldol polymer, that means once long chain higher molecular weight polymer were generated, they dissolve over a treatment of

antipolymerant. In this experiment, 0.021 moles VA were added in 40 mL of 10% caustic soda solution. The mixture was shaken vigorously at 350 rpm at 40°C. After a few minutes, the solution turned colorless to yellow. Yellowish orange precipitates were formed after 2 hours treated with different concentration of antipolymerant. The efficiency of dissolving efficiency measured by evaluating transmittance of each of the solutions by UV visible spectroscopy at 800 nm. A blank was also run simultaneously to compare the efficiencies of the additives and the transmittance of blank solution. The % transmittance (%T) was measured and is recorded in Table 3.

The dissolution performance of APTMS/APTES and SS-APTMS/SS-APTES were investigated and compared with SS-AHA and EA. The results found that as concentration of antipolymerant increases dissolution increases in APTMS/APTES and SS-APTMS/SS-APTES and SS-AHA. Overall SS-AHA found better at all VA:antipolymerant ratio except at 0.20 ratio SS-APTES found better %T. Moreover, at all higher to lower VA:antipolymerant molar ratio SS-AHA found almost similar %T, which exhibits both the amino and acidic group of long chain SS-AHA working highly effective for inhibition and dissolution at lower VA:antipolymerant ratio. Whereas Alkoxy group of the APTMS/APTES and SS-APTMS/SS-APTES is more effective at higher concentration of antipolymerant.

Table 3. Dissolution performance study of antipolymerant for aldol condensation reaction at different vinyl acetate (VA):antipolymerant ratios

No	VA: Antipolymerant ratio	% T at 800 nm on UV after 30 min					
		APTMS	***APTES***	***SS-APTMS***	***SS-APTES***	***SS-AHA***	***EA***
1	0.50	2	18	5	49	85	<1
2	0.33	5	47	19	77	86	<1
3	0.25	26	54	61	89	87	<1
4	0.20	35	60	56	98	89	<1

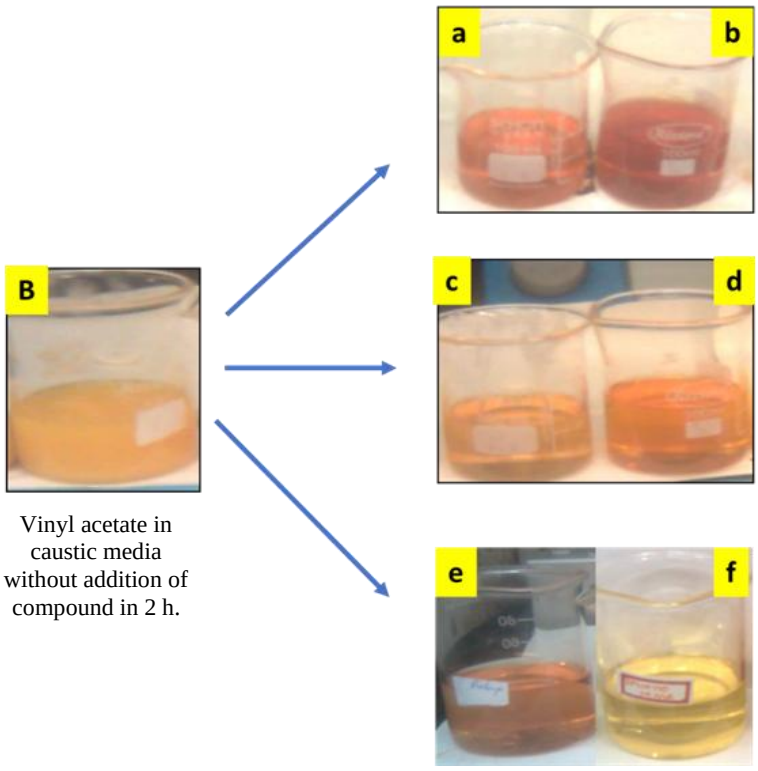
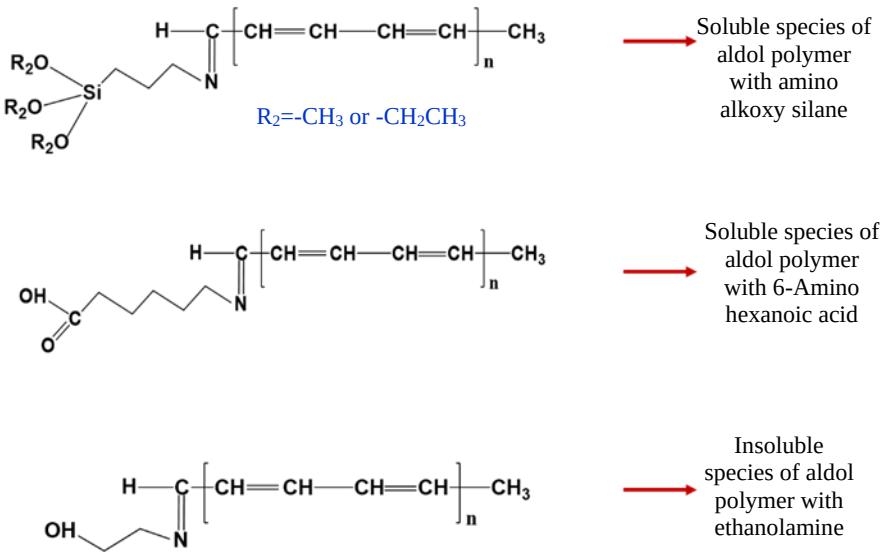


Figure 6. Inhibition performance of different antipolymerant after 2 hours. B: Vinyl acetate in caustic media without addition of antipolymerant at 40°C, (a) APTMS, (b) APTES, (c) SS-APTMS, (d) SS-APTES, (e) SS-AHA, (f) EA.

The results also found that higher chain alkoxy based amino silane showed better dissolution compared to small chain methoxy based amino silane. The EA found no effectiveness at all studied concentrations, which indicates that combination of -OH and -NH_2 group compound is not capable of dissolving aldol polymer (Scheme 5). It is possible that the presence of the amine group in Na salt of APTMS and Na salt of APTES helps in conversion of aldehyde to imine. Unlike aldehyde, imine does not undergo polymerization in alkaline media. Hence, the amine group appears to prevent aldol condensation. On the other hand, the Si-O-Na moiety of Na salt of APTMS and Na salt of APTES probably forms an adduct with the solid aldol polymers which facilitates dissolution of the aldol polymers in the alkaline medium. It is possible that Si-O-Na is more effective than the Si-O-alkyl moiety of pure APTES or pure APTMS because of the higher bond forming characteristics of Si-O-Na due to its ionic nature (Scheme 5). Thus, acidic group -COOH of amino acid and -OR group of aminoalkoxy silane essential for dissolution of aldol condensation polymer [19]. The appearance of dissolution of polymer after addition of antipolymerant is shown in Figure 7.

Table 4. Dissolution performance study of mix antipolymerant for aldol condensation reaction at different 0.25 vinyl acetate (VA):antipolymerant ratios.

Mixture of additives	Molar ratio of additives	VA: Antipolymerant ratio	% T at 800 nm on UV after 30 min
SS-AHA + SS-APTMS	90:10	0.25	80
SS-AHA + SS-APTMS	75:25	0.25	83
SS-AHA + SS-APTES	90:10	0.25	86
SS-AHA + SS-APTES	75:25	0.25	78
EA + SS-APTMS	90:10	0.25	5
EA + SS-APTMS	75:25	0.25	14
EA + SS-APTES	90:10	0.25	7
EA + SS-APTES	75:25	0.25	18
SS- APTMS	100	0.25	61
SS-APTES	100	0.25	89
SS-AHA	100	0.25	88
EA	100	0.25	<1



Scheme 5. Possible dissolution reaction of aldol polymer with different class of antipolymerant.

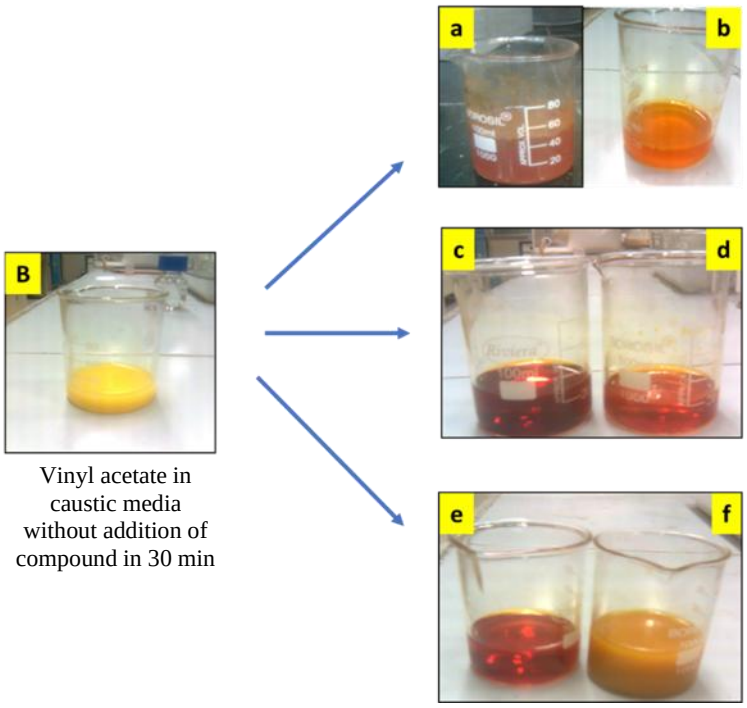


Figure 7. Dissolution performance of different antipolymerants after 30 minutes. B: Vinyl acetate in caustic media without addition of antipolymerant (a) APTMS, (b) APTES, (c) SS-APTMS, (d) SS-APTES, (e) SS-AHA, (f) EA.

Furthermore, dissolution of aldol polymer investigated using mixture of SS-AHA and EA with APTMS/APTES and SS-APTMS/SS-APTES at 90:10 and 75:25 antipolymerant ratios. All the reactions were conducted at 0.25 VA:antipolymerant molar ratio. The mixture of SS-AHA with SS-APTMS and SS-APTES indicates % T between 78 to 86 which is slightly lower compared to pure SS-AHA, indicates presence of aminosilane slightly decreases performance. Furthermore, mix antipolymerant dissolution with ethanol amine and SS-APTMS and SS-APTES found significantly decreased % T due to less effectiveness of EA for dissolution (Table 4). Thus, results exhibit that acidic -COOH and alkoxy group in the structure is essential for dissolution (Table 4).

CONCLUSION

Inhibition and dissolution behavior of acetaldehyde were studied using different compounds having -OR and -NH_2 functional groups. Compounds having higher basicity (electron donating groups) are efficient for inhibition of aldol reaction, but less effective as dissolution purpose. The compound with mixture of both alkoxy and amino group works for both inhibition of aldol condensation and dissolution of aldol polymer. Compared to all three categories of functionality, -compounds with COOH/-NH_2 and -OR/NH_2, are capable of inhibition and dissolution of aldol reaction, whereas -OH/NH_2 based compounds are only effective for inhibition.

REFERENCES

1. Caines LL, Shen SY. Energy and Environmental Systems Division Special Projects Group. Washington, DC, USA: U.S. Department of Energy; 1980. Contract W-31-1 09-Eng-38.
2. Bender M. An overview of industrial processes for the production of olefins–C_4 hydrocarbons. Chem Bio Eng Rev. 2014;1(4):136–47.
3. Seifollahi M, Forootan A, Reyhan SB. Examination of the reasons for the formation of red oil in spent caustic from olefin plant. World Acad Sci Eng Technol Int J Chem Mol Eng. 2016; 10 (8): 1162–1169.
4. Lewis VE. Method of inhibiting formation of fouling materials during basic washing of hydrocarbons contaminated with oxygen compounds. US Patent 5160425; 1992.

5. Lewis VE, Patel NR. Caustic tower trap for acetaldehyde. US Patent 5714055; 1998.
6. Lewis VE, Rowe CT. Process for the prevention of polymer formation in compressor systems. US Patent 5288394; 1994.
7. Tabler DC. Removal of carbonyls from polymerizable monomers. US Patent 3535399; 1970.
8. Awbrey SS. Method of inhibiting fouling in caustic scrubber systems. US Patent 4952301; 1990.
9. Gary P. Borohydrides to inhibit polymer formation in petrochemical caustic scrubbers. US Patent 5582808; 1996.
10. Roling PV. Method for prevention of fouling in a basic solution by addition of specific nitrogen compounds. US Patent 4673489; 1987.
11. Lewis VE, Rowe CT. Process for the prevention of polymer formation in compressor systems. US Patent 5288394; 1994.
12. Roling PV. Method for inhibiting fouling in caustic scrubber systems. US Patent 5194143; 1993.
13. Subramaniyam M, Prashant B. Method for prevention of fouling in basic solution by inhibiting polymerization and solubilizing deposits using amino acids. US Patent 6986839 B2; 2005.
14. Subramaniyam M. Method of removal of carbonyl compounds along with acid gases from cracked gas in ethylene process. US Patent 2005/0224394 A1; 2005.
15. Joseph S, Gondolfe M, Kurukchi SA. Eleventh Ethylene Forum, The Woodlands, TX, USA; May 14–16, 1997.
16. Wade LG. Organic Chemistry. 6th edition. Upper Saddle River, NJ, USA: Prentice Hall; 2005. Chapter 18, p. 804.
17. Zhu P, Chen X, Roberts CG. Method of use for aldehyde removal. US Patent 7041220; 2006.
18. Patil H, Bhajiwala H, Gupta V. A method of cracking petrochemicals. Indian Patent 1706/MUM/2011; 2011.
19. Bhajiwala HM, Patil HR, Gupta VK. Studies of amino acids for inhibition of aldol condensation and dissolution of polymeric product of aldehyde in alkaline media. Appl Petrochem Res. 2013; 3: 17–23.

