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STUDY OF AMINO-CONTAINING COMPOUNDS. ACID CORROSION INHIBITORS AND PRODUCTS OF THEIR DESTRUCTION DURING THE ABSORPTION PROCESS

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Abstract

Foaming of alkanolamine solutions is one of the main problems in the operation of installations for the purification of hydrocarbons and process liquids from acid gases. Foaming occurs most often in absorbers, less often in desorbers and manifests itself in a sharp increase in the volume of foam on the contact plates, an increase in the pressure drop in the apparatus, the appearance of liquid level in the purified or acid gas separator. The consequence of this is increased entrainment of the absorbent with gas and a decrease in the gas productivity of the installation. The purpose of this work was to assess the reactivity of compounds containing DEA, acid corrosion inhibitors.

Keywords: *gas, absorption, desorption, amines, oxides, water, corrosion, quantum chemical calculations, infrared spectroscopy*

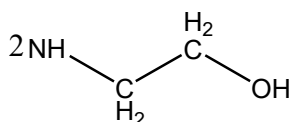
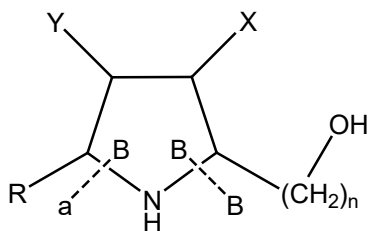
Introduction

The main reason for foaming, according to many researchers, is the result of the action of impurities that enter the absorber with gas, such as hydrocarbon condensate, formation water, sand, scale, iron sulfides, some corrosion inhibitors, and various surfactants. In this case, the effect of some impurities is manifested in an increase in the volume (height) of the absorbent foam (hydrocarbons); the action of others is to impart stability and rigidity to the foam (solid impurities); thirdly, in increasing the volume and

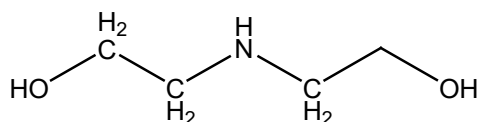
stability of the foam at the same time (surfactants, corrosion inhibitors such as “Visco”) (Attia N. F., Jung M., Park J., Jang H., Lee K., Oh H., 2020). We conducted studies during which it was revealed that iron sulfides and sand do not cause foaming of amine solutions, unlike acid corrosion inhibitors (ACI) and their decomposition products, which are polar substances and strong foaming agents. Process fluids contain a large number of ACI decomposition products that can interact with each other and with incoming (or escaping) gases (Cong Wang, Wenbo Jiang,

Guancong Jiang. Tonghuan Zhang. Kui He. Liwen Mu. Jiahua Zhu. Dechun Huang. Hongliang Qian. Xiaohua Lu.. (2023).

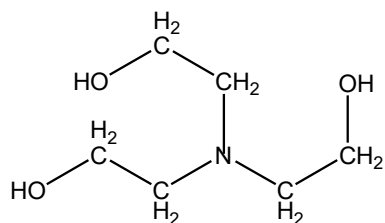
Gas condensate (GC) is an aggressive acidic environment. contains hydrocarbons. H_2S . CO_2 . mercaptans. etc. During the transportation of GC through pipes. in order to prevent corrosion of these pipes. acid corrosion inhibitors (ACI). which are a wide variety of amines. are added to the product. which are characterized by a general structure:



monoethanolamine (1)



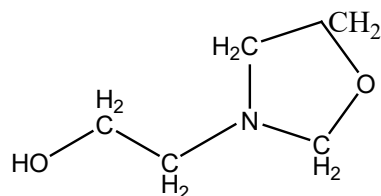
diethanolamine (2)



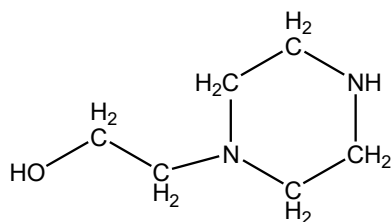
three ethanol amine (3)

During the amine purification of GC from H_2S and CO_2 . the interaction of DEA and TEA molecules with ACI occurs. both in the original state and in the form of their destruction

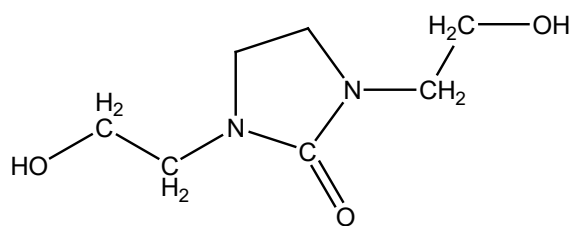
products. In this case. polar substances are formed. among which those whose formulas are given below are found.



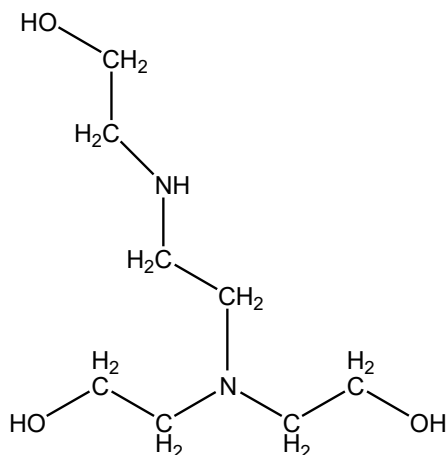
N-hydroxyethyl-α-azolidone (4)



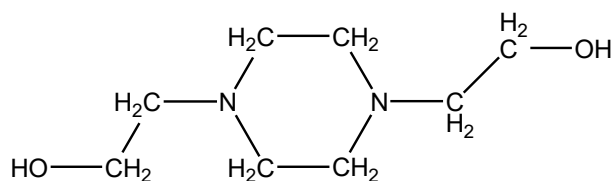
N-hydroxyethylpiperazine (5)



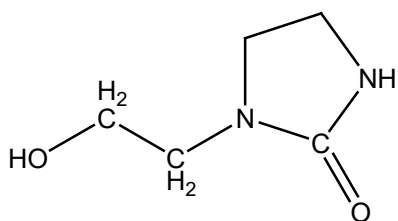
N,N-bis-oxyethylimidazoline (6)



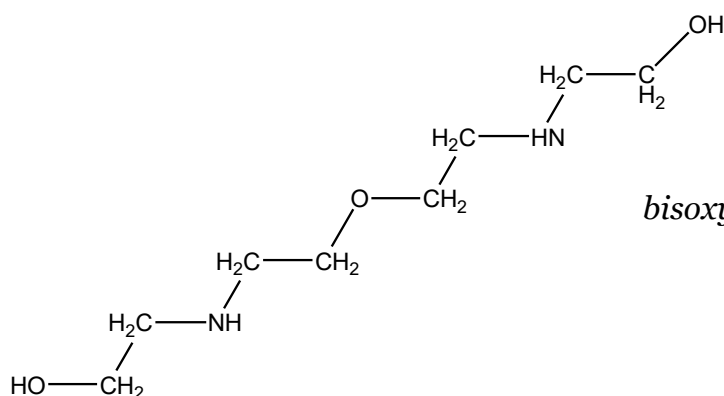
trihydroxyethylethylenediamine (7)



N,N-bis(2-oxyethyl)-piperazine (8)



N-hydroxyethylimidazolidone (9)



bisoxoethylaminoethyl ether (10)

Compounds (1), (4)–(8), (10) are classical nitrogen-containing cationic surfactants, highly soluble in water and involved in the formation of stable foam.

Compounds (5)–(10) also easily form ion pairs with H_2S or CO_2 and take part in liberating the environment from acid gases.

but both in the free state and in the form of compounds with H_2S or CO_2 they also form a stable foam.

Processes of nucleophilic and electrophilic substitution, electrophilic addition, intermolecular interactions, and condensation reactions are possible between alkanolamines.

their decomposition products. ACI and ACI decomposition products.

The purpose of this work was to assess the reactivity of compounds containing DEA, acid corrosion inhibitors (Dodigen, Hercules), as well as some fragments of ACI and compounds 5, 6, 8, 9, 10. Their reactivity was assessed using energy indices obtained using quantum chemical calculations.

Quantum chemical calculations were carried out in several software packages. The molecules were constructed in Chem Office-2004, and subsequent optimization and energy minimization, as well as refinement of geometric components and thermal characteristics, were carried out in Gamess (Rou Wang, Jianglong Yu, Faridul Islam, Arash Tahmasebi, Soonho Lee, Yixin Chen, 2020). The main calculation method is semi-empirical PM3 in the Hartree-Fock approximation. To solve the first problem, different states of each molecule were studied, taking into account their conformational diversity (Antonou M.K., Diamanti E.K., Enotiadis A., Po-

licchio A., Dimos K., Ciuchi F., Maccallini E., Gournis D., Agostino R.G., 2014; Caroline Thaler, Christian Millo, Magali Ader, Carine Chaduteau, François Guyot, et al., 2017).

The data on steric energy was processed, so all calculations were carried out on stable structures that have low heats of formation, which determines the potential energy of a state in molecular mechanics.

Due to the fact that many of the molecules under consideration have a similar structure and identical reaction centers, all structures are divided into groups. This division makes it possible to more accurately trace the activity of a particular group.

in a molecule. The first group includes molecules (1), (2), (3), (7), (10), the second - (5), (9), the third - (4), (6), (8).

Comparative analysis of the reactivity of compounds (1–10). In table Table 1 shows the charge values in structures (1–10). Based on these data, it is possible to trace the distribution of charges throughout the molecule as a whole.

Table 1. Distribution of charges in atoms of compounds (1–10)

Connection 1		Connection 2	
-N-	-0.0279	-N-	-0.0536
-O-	-0.3080	-O-	-0.3098
-H*	0.1830	-O*	-0.3094
-H**	0.0260	-H*	0.818
-C*	0.0638	-H**	0.0585
		-C*	0.0620
Connection 3		Connection 4	
-N-	-0.0935	-N-	-0.1185
-O-	-0.3071	-O-	-0.3115
-O*	-0.3145	-O*	-0.2788
-O**	-0.3070	-H*	0.1950
-H*	0.1895	-C*	0.0705
-H**	0.1915	-C**	0.0750
-C*	0.0669		
Connection 5		Connection 6	
-N-	-0.0672	-N-	-0.0658
-O-	-0.3035	-O-	-0.3052

Connection 1		Connection 2	
–N*–	–0.0570	–N*–	–0.0640
–H*–	0.0418	–O*–	–0.3005
–H**–	0.1795	–O**–	–0.3620
–C*–	0.0575	–H*–	0.1875
		–H**–	0.1852
		–C*–	0.0385
		–C**–	0.2517
Connection 7		Connection 8	
–N–	–0.0715	–N–	–0.0660
–O–	–0.3145	–O–	–0.3058
–N*–	–0.0579	–N*–	–0.0453
–O*–	–0.3109	–O*–	–0.3577
–O**–	–0.3165	–H*–	0.0910
–H*–	0.1857	–H**–	0.1856
–H**–	0.1980	–C*–	0.0599
–H***–	0.0470	–C**–	0.2335
–C*–	0.0389		
–C**–	0.0775		
Connection 9		Connection 10	
–N–	–0.0876	–N–	–0.0500
–O–	–0.3120	–O–	–0.3025
–N**–	–0.0745	–N*–	–0.0680
–O*–	–0.3060	–O–	–0.2645
–H*–	0.1820	–O*–	–0.3120
–H**–	0.1945	–H*–	0.0635
–C**–	0.0560	–H**–	0.1950
		–C*–	0.0665

The main reaction centers are considered to be –OH, –NH₂, –NH, > C = O groups. In order to simulate the possible behavior of a molecule in any medium (solvent), as well as to identify the main area of the contact sur-

face, the energy characteristics of compounds (1) – (10) were calculated, as well as the areas of the contact surfaces, the values of which are given in Table 2.

Table 2. Energy characteristics of compounds

No	ΔG° , kJ/mol	ΔH° , kJ/mol	Area of test sphere A_1	Contact area surfaces A_2	Solvent volume	E_{steric} , kJ/mol
1	–104.40	–215.20	202.00	80.00	55.00	18.22
2	–201.38	–419.02	274.22	124.12	95.10	104.00

No	ΔG° . kJ/mol	ΔH° . kJ/mol	Area of test sphere A_1	Contact area surfaces A_2	Solvent volume	E_{steric} . kJ/mol
3	-300.00	-625.12	283.00	165.02	131.25	161.00
4	-64.75	-375.00	245.00	136.00	103.00	15.55
5	106.00	-217.00	267–55	152.47	121.00	66.36
6	-99.02	-581.32	311.45	183.00	145.36	64.25
7	-194.82	-624.33	351.45	211.22	175.00	111.33
8	-13.40	-380.00	248.00	138.36	104.24	45.00
9	20.76	-417.85	328.00	195.00	131.23	97.85
10	-183.40	-600.95	363.42	216.00	171.00	26.04

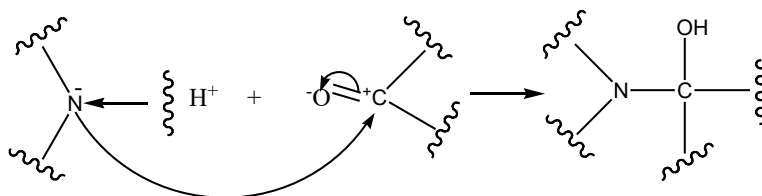
Legend: ΔG° . kJ/mol – standard Gibbs energy. at $T = 298$ K; ΔH° . kJ/mol – standard heat of formation of a molecule from simple compounds at $T = 298$ K; A_1 is the area of the test sphere occupied by the solvent when rolling over the surface of the molecule under study; A_2 is the area of the contact surface that occurs during rolling research on the surface of the molecule under study; A_3 is the volume of solvent contained inside the contact surface; E_{steric} . kJ/mol – steric energy. used to describe the thermal motion of atoms of a molecular system (Coplen T. B., 2007)

From the table 2 it can be seen that the contact surface area of N,N-bis-oxyethylimidazoline is higher than in the structure of N-oxyethylimidazolidone. This is primarily due to the presence of a linear branched carbon skeleton. with in this case. the volume of solvent contained inside the contact surface increases proportionally. A similar effect can be observed in the structures of the second group: thus. the N, N-bis-(2-oxyethyl)-piperazine molecule will be maximally involved in the solution. and to a lesser extent. N-hydroxyethylpiperazine.

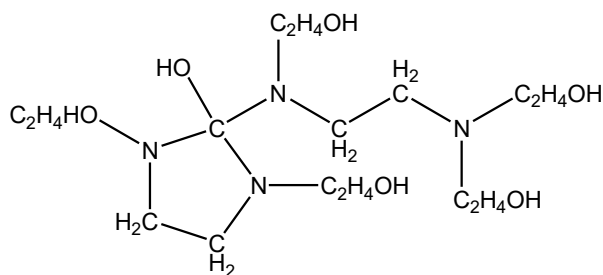
If we talk about the reactivity of N-hydroxyethylpiperazine. then it is necessary to note the weak influence of the imide group. and the largest contribution is made by the hydroxo group. through which electrophilic substitution can occur. as well as participation in the formation of hydrogen bonds. In the first group. structures (7) and (10) have the maximum contact surface area; this is also due to the branched carbon skeleton.

The maximum accumulation of negative charge on the nitrogen atom is observed in the three ethanol amine molecule ($\rho = -0.0933$). which indicates the presence of a nucleophilic attack center. but steric hindrances associated with the location radicals in the molecule make it difficult to introduce other agents. so three ethanol amine occupies an intermediate position in this group in terms of its ability to interact.

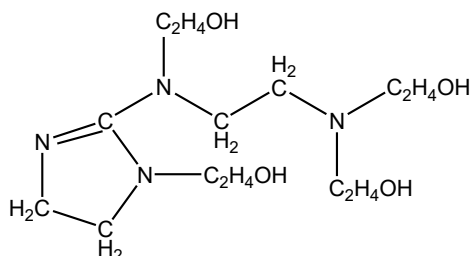
A similar state is characteristic of trioxyethylethylenediamine. but in this case the participation of the $-NH$ group can make its own contribution to the nucleophilic attack. while the average value of the charges on the nitrogen atom is -0.065 and this is lower than for the three ethanol amine molecule. so one would expect a decrease in the reactivity of trioxyethylethylenediamine. But. having a branched linear structure. molecules (7) and (10) turn out to be the most active in this series. therefore they are able to react to form nitrogen-containing colored compounds:



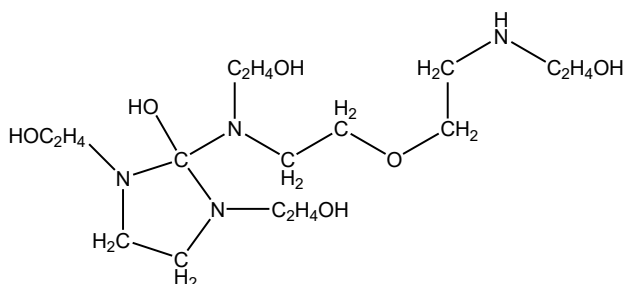
As a result of such interaction. the formation of the following compounds is possible:



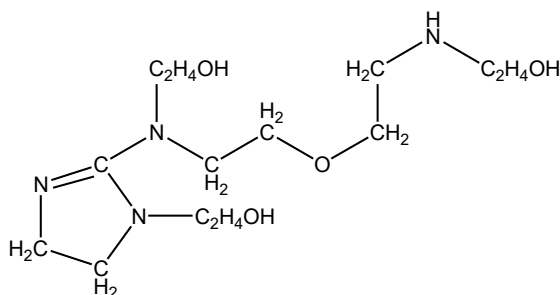
reaction product between
(7) and (6) (11)



product of the reaction
between (7) and (8) (12)



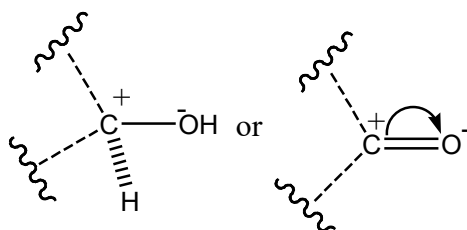
reaction product between
(10) and (6) (13)



reaction product between
(10) and (8) (14)

The maximum contribution to the reactivity is also made by the electrophilic centers of terminal carboxyl radicals and carbonyl

groups. therefore, such compounds are characterized by nucleophilic substitution reactions:



The -NH group, which is capable of participating in addition reactions and the formation of nitrogen-containing colored products, has less activity; molecules (7) and (10) are prone to this effect; Identification of reaction centers made it possible to find out how all molecules will behave in a common active liquid-vapor environment: in relation

to each other; in relation to gases entering (or released) into the system.

Calculations show that most of the individual substances considered can be the cause of intense foaming. One of the reasons may be the formation of compounds of the studied substances with hydrogen sulfide and other acid gases.

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