INFLUENCE OF ALKYLATED NAPHTENİC ACID AMIDE CONTAINING BIOCIDE COMPOSİTİONS OF BAKU CRUDE OIL ON SULPHATE REDUCING BACTERIA

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Compounds formed in the reaction of napthenic acid amides of Baku crude oil with some of the alkyl halogenides are found to be multi-functional corrosion inhibitors. The structural features of compounds were studies with FT-IR spectroscopy. The efficiency of these inhibitors have also been tested against sulphate reducing bacteria (SRB) at 30 ^{o}C for and for a period of 15 days time.

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INTRODUCTION

Corrosion of metals causes significant economic losses in the oil and gas industry all over the world.[1-3] Despite the development of various methods, latest chemical technology and inhibitory protection, corrosion of metals still remains a serious and critical problem. Approximately 77-80 % of the accidents occurred in oil and gas industries were due to biocorrosion.[4-6] Bio-damage is a typical failure of metallic structures and is due to destructive effect of microorganisms and their metabolic products towards metals. The mechanisms of bio-damage basically depend on the characteristics of the metal as well as other bio-factors. Crude oil is considered to be a mixture of hydrocarbons, which is not an optimum medium for the development of microorganisms, however, water of simulated oil field enriched by sulfur compounds is favorable ecosystem for the development of sulphate reducing bacteria (SRB).[7-9]

The majority of the problems in the oil and gas industries are the result of insistent technological environment caused by hydrogen sulfide (H_2S) and carbon dioxide (CO_2). Formation of H_2S and its concentration is mainly associated with the existence of SRB's.

Corrosion problems occurr due to the presence of carbon dioxide in the oil. Inspite of various efforts and investigations on corrosion problems by carbon dioxide is still a serious problem of the oil and gas industry all over the world.[10-19] In the oil extraction and processing industries, corrosion inhibitors are considered as the front line defense against corrosion. In recent times, most of the inhibitors used in producing oil wells have been organic nitrogen compounds.

Presently, the bactericide behavior of some compounds (and their mixtures) synthesized from the reaction of amides with alkyl halogenides are investigated and reported. The results show that, the synthesized compounds are good inhibitors against SRB's activity.

EXPERIMENTAL

The compounds formed in alkylation of amides with alkylhalogenides were synthesized from the amides of naphthenic acids obtained from Baku crude oil.[20] Amides were synthesized from polyethylene polyamine and naphthenic acids from Baku crude oil and then these synthesized-amides were alkylated with the alkyl halogenides such as: $C_5H_{11}Br$; C_3H_7Br; C_6H_5Cl; C_4H_9Cl; $C_8H_{17}Br$; $C_5H_{11}Cl$ (iso); $C_6H_{13}Cl$ following the standard procedures.

The sructures of the synthesized amides and their alkylated compounds were identified by physico-chemical and spectroscopic methods (Table 1).

Infrared spectra for the synthesized compounds were obtained using a Spectogram on BX FT-IR spectrometer using KBr disks.

RESULTS AND DISCUSSION

Influence of synthesized compounds on the activity of SRB in a period of 15 days time

SRB is an obligate anaerobic bacterium which converts sulphates into H_2S. One of the most optimal cultural medium for growth of SRB is Postgate B. The compositions of this medium are recorded in Table 2. The parameters were calculated and given for 1 litre of solution. The pH was adjusted between 7.0 and 7.5.

Table 1. Physical-chemical properties of imidazoline compounds with alkyl halogenides

Compounds code name and composition		Molar ratio	Density, d_4^{20}, g cm^{-3}	Refraction coefficient, η_{20}^D	Freezing temperature, ^{0}C
F-1	amide and C_3H_7Br	1:1	0.9268	1.4300	-53
F-2	amide and C_3H_7Br	1:2	0.9288	1.4340	-52
F-3	amide and C_3H_7Br	1:3	0.9296	1.4310	-60
F-4	amide and $C_5H_{11}Br$	1:1	0.9124	1.4160	-60
F-5	amide and $C_5H_{11}Br$	1:2	0.9298	1.4330	-60
F-6	amide and $C_5H_{11}Br$	1:3	0.9314	1.4330	-60
F-7	amide and C_6H_5Cl	1:1	0.9664	1.4400	-40
F-8	amide and C_6H_5Cl	1:2	0.9788	1.4460	-50
F-9	amide and C_6H_5Cl	1:3	1.0381	1.4680	-58
F-10	amide and C_4H_9Cl	1:1	0.9269	1.4600	-56
F-11	amide andC_4H_9Cl	1:2	0.9500	1.4710	-56
F-12	amide and C_4H_9Cl	1:3	0.9750	1.4760	-56
F-13	amide and $C_8H_{17}Br$	1:1	0.9600	1.4550	-56
F-14	amide and $C_8H_{17}Br$	1:2	0.9700	1.4470	-56
F-15	amide and $C_8H_{17}Br$	1:3	0.9900	1.4520	-52
F-16	amide and $C_5H_{11}Cl$ (iso)	1:1	0.8650	1.4160	-56
F-17	amide and $C_5H_{11}Cl$ (iso)	1:2	0.8700	1.4110	-56
F-18	amide and $C_5H_{11}Cl$ (iso)	1:3	0.8700	1.4160	-56
F-19	amide and $C_6H_{13}Cl$	1:1	0.8480	1.4050	-56
F-20	amide and $C_6H_{13}Cl$	1:2	0.8500	1.4100	-56
F-21	amide and $C_6H_{13}Cl$	1:3	0.8800	1.4200	-56

Table 2 The composition of Postgate B cultural medium

Name of substance	Amount, g
Potassium phosphate (KH_2PO_4)	0.5
Ammonium chloride (NH_4Cl)	1.0
Calcium sulfate ($CaSO_4$)	1.0
Magnesium sulfate ($MgSO_4{\cdot}7H_2O$)	2.0
Sodium lactate	3.5
Sodium chloride	2.0

Cultural medium was optimized by the addition of special additives into the medium. Further additives used were: $FeSO_4{\cdot}7H_2O$ (5 % iron sulfate in 2% hydrochloric acid solution), sodium bicarbonate $NaHCO_3$ (5 % solution), crystalline $Na_2S.9H_2O$ (1 % sodium sulfide in 1 % sodium bicarbonate ($NaHCO_3$) solution).

SRB 1143 strain has been used in the experiments under test. Pre-sterilized test tubes (20 ml volume) were used.[21] Bactericide effects of the reagents have been tested over a 15 days period and calculated from the amount of the generated H_2S. H_2S was determined iodometrically by a standard method. Effects of compounds on the activities of SRB in concentrations of 0.025; 0.075 and 0.1 % are shown in the Table 3. It may be seen from the Table 3 that compounds synthesized from the reaction of amides with C_3H_7Br in molar ratio 1:1 (F-1) and 1:2 (F-2) showed biocide activity even at concentration of 0.025; 0.075 and 0.1 % and could stop the activity of the SRB.

The compound synthesized from amide and C_3H_7Br using 1:3 molar ratio (F-3) in concentration of 0.025 % showed a biostat effect i.e. showed a weak effect to life activities of SRB. But in concentration of 0.075 % and 0.1 % had the effect of biocide. The compound synthesized from amide and $C_5H_{11}Br$ using 1:1 molar ratio (F-4) had the effect of biocide in all concentrations, but the compound obtained using 1:2 molar ratio of amide and $C_5H_{11}Br$ (F-5) in concentration of 0.025 % and 0.075 % has biostat effect on SRB at 0.1 % concentration. The compound from the amide and $C_5H_{11}Br$ at molar ratio of 1:3 (F-6) has biocide effect. Among compounds from amide:C_6H_5Cl in molar ratio of 1:1 (F-7); 1:2 (F-8) and 1:3 (F-9), the compounds F-7 and F-8 showed biostat effects on SRB's life activity in 0.025 % concentration, and biocide effect at concentrations of 0.075 % and 0.1 %. Compound F-9 has biocide effect at all concentrations. The compounds from amide and C_4H_9Cl in 1:1 (F-10) and 1:2 (F-11) molar ratio were shown effect of biocide to life activity of SRB. But the compound synthesized from amide and C_4H_9Cl (F-12) in 1:3 molar ratio showed biostat effect in concentration of 0.025 %, but proved to be biocide at all other concentrations.

The compounds synthesized from amide and $C_8H_{17}Br$ in molar ratio 1:1 (F-13); 1:2 (F-14); 1:3 (F-15) has stopped life activity of SRB at all concentrations. The compound F-16 from 1:1 molar ratio of amide and iso-$C_5H_{11}Cl$ () was biocide in all concentrations, those from molar ratios of 1:2 (F-17) and 1:3 (F-18) showed biostat effects in concentration of 0.025 %, but showed biocide effects in 0.075 % and 0.1 % concentrations on SRB. The compounds from amide and $C_6H_{13}Cl$ in molar ratio 1:1 (F-19); 1:2 (F-20); 1:3 (F-21) stopped life activity of bacteria in all concentrations. Control 1 is a culture media without SRB, but control 2 is a culture media with SRB. As can be seen from the Table 3 that no culture grew in the control 1, butthe generated content of H_2S in the control 2 was 270 mg L^{-1} due to SRB growth.

Therefore, the compound F-4 (amide:$C_5H_{11}Br$, in molar ratio 1:1) showed the most powerful bactericidal efficiency.

Table 3. Effect of compounds on the life activities of SRB

Compounds code name and initiative matter	Molar ratio	Compound concentration, %		
		0.025	0.075	0.1
		H_2S content, mg L^{-1}		
(F-1) amide:C_3H_7Br	1:1	29	28	25
(F-2) amide:C_3H_7Br	1:2	30	26	25
(F-3) amide:C_3H_7Br	1:3	85	28	27
(F-4) amidee:$C_5H_{11}Br$	1:1	26	25	25
(F-5) amide:$C_5H_{11}Br$	1:2	85	83	28
(F-6) amide:$C_5H_{11}Br$	1:3	51	28	27
(F-7) amide:C_6H_5Cl	1:1	86	27	26
(F-8) amide:C_6H_5Cl	1:2	87	25	25
(F-9) amide:C_6H_5Cl	1:3	27	27	26
(F-10) amide:C_4H_9Cl	1:1	28	26	25
(F-11) amide:C_4H_9Cl	1:2	27	26	25
(F-12) amide:C_4H_9Cl	1:3	196	30	27
(F-13) amide:$C_8H_{17}Br$	1:1	28	27	25
(F-14) amide:$C_8H_{17}Br$	1:2	30	27	26
(F-15) amide:$C_8H_{17}Br$	1:3	27	26	25
(F-16) amide:$C_5H_{11}Cl$-i	1:1	27	26	25
(F-17) amide:$C_5H_{11}Cl$-i	1:2	187	28	26
(F-18) amide:$C_5H_{11}Cl$-i	1:3	127	26	25
(F-19) amide:$C_6H_{13}Cl$	1:1	28	26	25
(F-20) amide:$C_6H_{13}Cl$	1:2	27	26	25
(F-21) amide:$C_6H_{13}Cl$	1:3	28	26	25
Control 1 (culture media without SRB)	25			
Control 2 (culture media, with SRB)	270			

Chemical structure of the synthesized amidoalkyhalogenide compounds

The structural characteristics of purified product were confirmed by FT-IR spectroscopy in the range 4000–500 cm^{-1}, as shown in Fig. 1. IR spectrum of sample F-4 contains a series of absorption bands of varying intensity in the region 500-4000 cm^{-1}. In addition, there was a band at 729.57 cm^{-1} indicating the presence of the pendular oscillations of C-H bond in CH_2 group. The band bending at 1377.13 sm^{-1} and stretching vibrations at 2862.24, 2955.60 cm^{-1}, are characteristic for the C-H bond of the methyl (CH_3) groups. The absorption bands of strong intensity of deformation at 1377.13 cm^{-1} and stretching vibrations at 2862.24, 2955.60 cm^{-1} are characteristic for the C-H bond of the methylene (CH_2) groups. Carbonyl absorption band of N-acyl groups at 1550.00, 1643.55 and 1731.65 cm^{-1} are observed in several bands lower and upper frequency. Additionally, stretching band at 2356.97 cm^{-1} is due to NH_2 group. There are absorption bands at 814.65, 951.16, 1289.32 cm^{-1} in spectrum are characteristic for the corresponding C-H bond. Stretching band at 2335.01, 2356.97 cm^{-1} are due to NH_2 group. Stretching bands at 1047. 86, 1097.25 cm^{-1} are characteristic for the O−H bond of the OH groups. There are absorption bands of strong intensity of stretching vibrations at 505.68, 528.65, 544.00, 578.00 cm^{-1} which are characteristic of the C−Br bond.

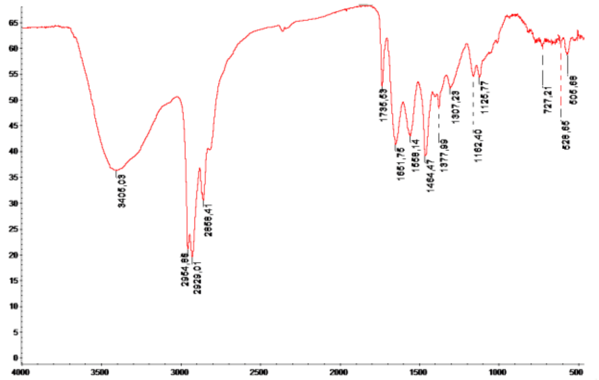

Figure 2. IR Spectrum of the **F-4** compound.

SUMMARY

The following conclusions are drawn from the present study:

SRB's 1143 strain have been used in tests to study the bactericide efficiency of friendly compounds of amidoalkylhalogenides synthesized on the bases of naphthenic acids fom Baku crude oil.

The structures of synthesized compounds were confirmed by physico-chemical and spectroscopic methods.

All synthesized compounds showed bactericidal effect as biostat and biocide.

It has been identifide that synthesized compound of amide uing $C_5H_{11}Br$ in molar ratio of 1:1 (F-4) stopped the life activities of SRB in consentrtions of 0.025; 0.075 and 0.1%. It has a stronger bactericide efficiency than could be observed in other compounds.

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