



Research on the Influence of Quaternary Ammonium Salts on Corrosion of Oil and Gas Field Equipment

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ABSTRACT: It is shown, that corrosion inhibitors on the basis of monomeric quaternarydivinyl salts N, N-dialkylaminoethylacrylatechlorides with vinylbenzilebromide (ABC) simultaneously are hydrogenation inhibitors of carbonaceous steel in the environments saturated with hydrogen sulfide and carbonic gas both separately, and in common at corrosion potential and under conditions of anode and cathode polarization.

KEYWORDS: hydrogenation,quaternary ammonium salt, corrosion inhibitor, adsorbed hydrogen, rate of diffusion, corrosive environment.

I. INTRODUCTION

Metals hydrogenation – rather widespread phenomenon leading to essential change of their physical and chemical characteristics: the volume of crystal lattice changes, there are mechanical stresses, hydrogen embrittlement and, as result, cracks. Inherently of the existing concept of hydrogenation the complex of the physical and chemical phenomena on interface of phases lays: adsorption of hydrogen atoms on metal surfaces, its dissolution in near-surface layers and metal volume, interaction with defects of structure, increase of anode activity owing to increase in deficiency of metal structure and occurrence of internal stresses, etc. causes acceleration of corrosion processes [1,2,4-7].

II. LITERATURE SURVEY

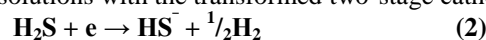
It is earlier established, that carbon dioxide corrosion is not accompanied by hydrogen embrittlement as carbon dioxide, unlike hydrogen sulphide, not slowdown process of hydrogen molization. Hydrogen sulphide presence in oil-field systems increases simultaneously both speed of hydrogen release, and its penetration into metal in cathode area of potentials, and the share of the hydrogen penetration into metal, increases with potential reduction [5,6].

It can be considered as result of presence of one-electronic transitions on border metal-electrolyte with formation or decomposition of dimeric hydrogen containing components in the form of stable or intermediate products [7]:

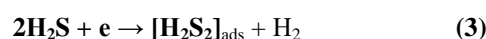
- Course of cathode reaction with participation of hydrogenation as intermediate product that is proved by the theory of electrochemical desorption



- Electrolysis of sour sulphide solutions with the transformed two-stage cathode reaction



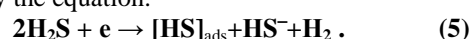
stage of one-electronic transition



chemical stage



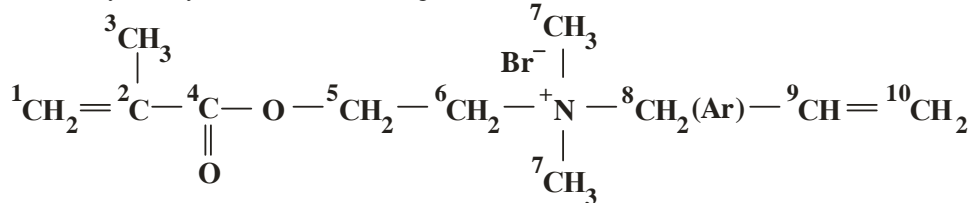
- Totally process is described by the equation:



The greatest efficiency of action of hydrogen sulfide as stimulator of hydrogenation in sour environments is shown in small anode potential displacement: practically completely suppresses hydrogen release in gas phase, but considerably increases its penetration into metal [6,7].

Inhibitors of acid and hydrosulphuric corrosion (CI) in various degrees slow down processes of hydrogenation. However, as a result of influence of some factors (pH environments, temperature, polarization degree, etc.) a change of chemical compound and a structure of inhibitors molecules is possible, that causes transfer of hydrogen ions of inhibitory process and restoration process from one stage to another that make possible transformation of inhibitors in stimulators and backwards [7].

In this connection represents scientific and practical interest research of influence on process of hydrogen diffusion to steel CI based on functional-active compounds – monomeric quaternary divinyl salts N, N – dialkylaminoethyl acrylate chlorides with vinyl benzyl bromide (ABC) of general formula [2,3]:



III. EXPERIMENTAL RESULTS

The studying of surface-active properties spent with water solutions by a method of electro capillary curves, has shown, that in considered area of concentrations ABC of an isotherm of electro conductivity have nonlinear character (Fig. 1). It can be caused by action of two factors: at dilution of aqueous solutions MCC-M and MCC-E a share of free counter ions, participating in transfer of electricity and simultaneously the total charge of macroions and, as consequence, its mobility grows that is second factor promoting increase in equivalent electroconductivity of a solution [2,3].

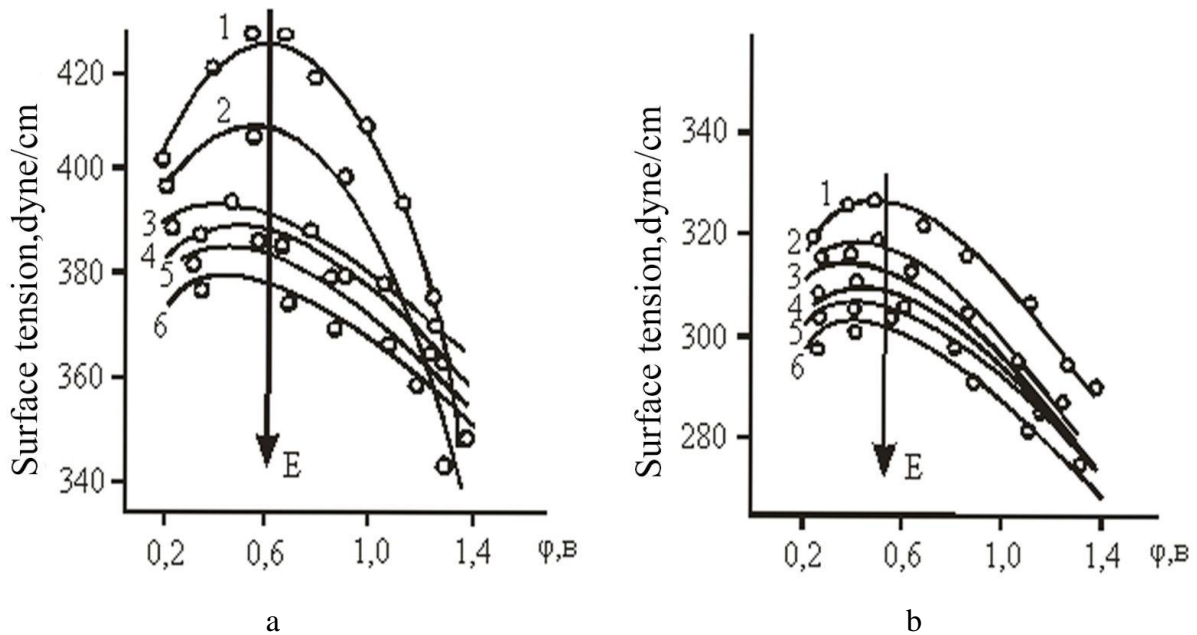


Fig 1. Dependence of surface stress on ABC content (mole/l) MCC-M(a) and MCC-E(b)
 a- 1-background 0,1n NH₄CL; 2- 3,1·10⁻⁵; 3- 3,1·10⁻⁴; 4-9,0·10⁻⁴; 5-2,04·10⁻³; 6-4,06·10⁻³
 b- 1-background 0,1n NH₄CL; 2- 2,8·10⁻⁵; 3- 2,8·10⁻⁴; 4-7,4·10⁻⁴; 5-1,4·10⁻³; 6-2,8·10⁻³

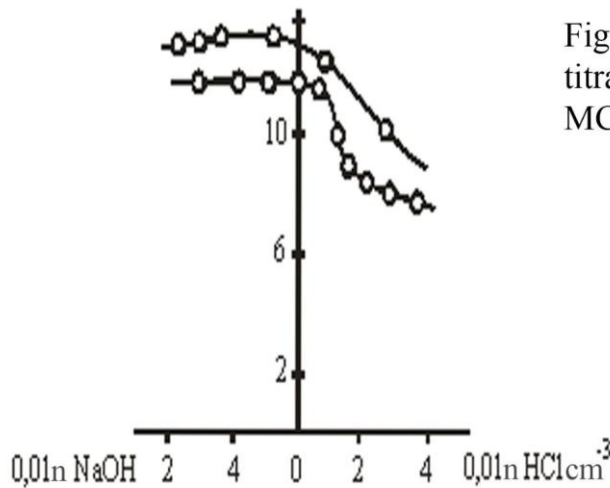


Fig.2. Curves of electrometric titration ABC MCC-V(1) and MCC-E(2)

By potentiometric titration (Fig 2.) it is established, that in the presence of ABC sharp decrease in values of superficial tension of (σ) mercury is marked and the maximum of electro capillary curves is displaced to more positive potentials, showing cation activity ABC.

Adsorption of molecules ABC occurs, presumably, at the expense of π -electronic interaction of double connections with surface of mercury. Rather high value of superficial activity is inherent to MCC-M that is caused, apparently, by steric effect.

It is experimentally established, that with increase of concentration of MCC-M more intensively, decreases a superficial tension of mercury and (Fig. 1, a) and superficial concentrations of the adsorbed molecules (Tab. 1) raise.

Table 1- dependence of adsorption characteristics MCC-M on solution concentration

Concentration of the solution, mole/l	Drop of surface stress, $n/m \cdot 10^{-7}$	Concentration of adsorbed molecules, $mole \cdot 10^{-10}/m \cdot 10^{-10}$
$3,1 \cdot 10^{-5}$	16	$1,19 \cdot 10^{-10}$
$3,1 \cdot 10^{-4}$	36	$2,38 \cdot 10^{-10}$
$3,1 \cdot 10^{-5}$	46	$2,60 \cdot 10^{-10}$

Stopping power ABC already at the content of 10 mg/l is effective as for BNE, and gas condensate. Decrease of stopping power ABC with content increase in system is caused, apparently, by processes of globulization as a result of conditional surplus presence of function-active groups.

Thus, established surface-active properties ABC allow considering them as potential corrosion inhibitors for systems, a working environment for which is hydrogen sulfide containing hydrocarbons (water-oil emulsions, gas condensate, etc.).

Research of hydrogen mass transfer was spent at room temperature by known technique [6, 8] with use of 0,01 n solution of potassium permanganate, expressing in terms of current density quantity of diffused through steel membrane of hydrogen.

Influence on process of hydrogen diffusion in steel is considered in 0,001-0,1M solutions HCl in the presence of carbonic gas, hydrogen sulfide (background media) and CI (corrosion inhibitor) at corrosion potential, and also cathode polarization of a steel membrane. Table 2 presents data on stimulation of a steel hydrogenation at introduction of carbonic gas and hydrogen sulfide. The effect of stimulations is conditioned by general rate of corrosion and quantity of the adsorbed hydrogen (H_{ads}), leading to growth of degree of filling of the adsorbed centers by atoms of

hydrogen (Θ_H) and, as consequence, to more intensive penetration of hydrogen into metal. Along with it a delay of recombination of the adsorbed atoms of hydrogen and stimulation of hydrogenation is possible.

Table 2 – influence of environment composition on rate of hydrogen diffusion through a membrane (i_H) and stimulation factor (β) in background solutions ($\tau = 2$ hour, $t = 22,5$ °C)

Concentration of the solution, C_{HCl} , mole/l	Solution composition $C_{CO_2} = 1,5$ g/l, $C_{H_2S} = 50$ mg/l	i_H A/m ²	β (i/i_0)
0,1	HCl	0,32	1,00
	HCl+CO ₂	0,35	1,07
	HCl+H ₂ S	0,66	1,62
	HCl+CO ₂ +H ₂ S	0,52	1,40
0,01	HCl	0,20	1,00
	HCl+CO ₂	0,22	1,05
	HCl+H ₂ S	0,54	2,51
	HCl+CO ₂ +H ₂ S	0,48	2,07
0,001	HCl	0,17	1,00
	HCl+CO ₂	0,19	1,08
	HCl+H ₂ S	0,48	2,32
	HCl+CO ₂ +H ₂ S	0,32	1,51

Introduction CO₂ in hydrogen sulfide containing media leads to decrease in rate of diffusion of hydrogen through a membrane (i_H), that is conditioned, apparently, by competitive adsorption of carbonic gas and hydrogen sulfide though carbonic gas is a passive stimulator of hydrogen diffusion in a steel.

Influence CI on hydrogen diffusion to steel is presented in table 3. It is obvious, that ABC in all tested solutions shows effective inhibitory action on suppression of hydrogen diffusion through steel membrane (γ_n) at low enough content system. It is obvious, that introduction in ABC in system effectively raises suppression of hydrogen diffusion through a membrane in the presence of stimulators of hydro permeability and causes the greatest effect in hydrogen sulfide media. Influence ABC on hydrogenation, apparently, has the complex character including following processes:

- Decrease in quantity of formation of the adsorbed hydrogen (H_{ads});
- Blocking by the adsorbed particles ABC of the recombination and hydrogen removals into gas phase;
- Change of diffusion factor of the atomic hydrogen defined by the nature and the thickness of a salt blanket on which partial electrode reaction are localized and through which H_{ads} diffuses deep into metal.

Table 3 – Influence ABC on suppression factor of hydrogen diffusion through a membrane (γ_n) ($\tau = 2$ hour, $t = 22,5$ °C)

Concentration of the solution, C_{HCl} , mole/l	Solution composition $C_{CO_2} = 1,5$ g/l $C_{H_2S} = 50$ mg/l	γ_n at concentration ABC, mg/l		
		15	20	35
0,1	HCl	1,35	1,60	3,81
	HCl+CO ₂	1,42	1,52	4,01
	HCl+H ₂ S	3,52	3,61	3,75
	HCl+CO ₂ +H ₂ S	2,75	2,83	2,91
0,01	HCl	1,15	1,50	3,81
	HCl+CO ₂	1,31	2,50	3,79
	HCl+H ₂ S	3,05	3,15	3,62
	HCl+CO ₂ +H ₂ S	2,50	2,71	2,85
0,001	HCl	1,05	1,60	3,81
	HCl+CO ₂	1,25	2,42	3,52
	HCl+H ₂ S	2,87	2,99	3,32
	HCl+CO ₂ +H ₂ S	2,65	2,71	2,79

The factors specified above promote change of concentration of atomic hydrogen in near-surface, i.e. degree of filling of a surface by adsorbate Θ_H : potential inhibitors of hydrogenation lead to reduction Θ_H .

According to [4, 5, 7] exist energetically differing above-surface (H^r) and subsurface (H^s) types of the adsorbed hydrogen atoms: H^r is responsible for hydrogen removal in gas phase, and H^s –for adsorption by metal. Balance is observed at:



In case of inhibition balance (6) is displaced to the left, i.e. in area of formation of above-surface, passing in gas phase of hydrogen. Also H_{ads} can move off in gas phase as a result of recombination: if at a general increase Θ_H^r inhibitor will intensively stimulate formation of molecular hydrogen, simultaneously it will short-stop hydrogenation [7-9].

Fig. 3 presents microphotos of samples (steel 20), made on metallurgical microscope Neofot-21 and within 30 days subjected to influence of the standard test aggressive salt solution presented above composition with content of hydrogen sulfide 3 g/l and 50 mg/l gas condensate.

The sample that was in corrosive environment (Fig. 3a.) without ABC, has manifests of corrosion traces along lines of rolled steel banking. The sample that was in inhibited MCC-M (25 mg/l) environment, has no even corrosion traces that testifies to inhibitory film-forming effect ABC.

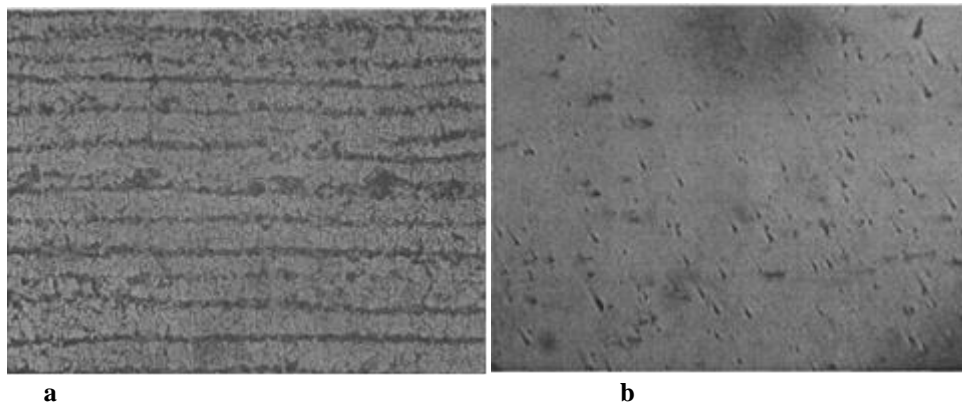


Fig. 3. Microphotos of check test pieces after medium impact, of no inhibited (a) and inhibited ABC (b)

IV. CONCLUSION

Thus, it is established, that corrosion inhibitor based on quaternary ammonium salts ABC causes suppression of steel hydrogenation in carbon-dioxide-hydrogen sulfide containing environments that is caused, apparently, by presence of quaternized atom of nitrogen participating in replacement of the adsorbed stimulating particles as a result of competitive adsorption.

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