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> ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

# New Integrated-Action Oilfield Reagent Having Properties of Scaling Inhibitor and Hydrogen Sulfide Neutralizer

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Abstract—Method for obtaining a new oilfield reagent for inhibition of scaling and neutralization of hydrogen sulfide on the basis of paraformaldehyde, monoethanolamine, and phosphorus(V) oxide was developed.

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The scaling and the increased content of hydrogen sulfide and mercaptans pose severe problems in development and operation of oil-and-gas wells [1-4]. The scaling process is directly associated with the strong supersaturation of the aqueous medium with difficultly soluble salts because of the change in the physicochemical parameters of the oil extraction system (temperature, pressure, gas evolution, concentration of precipitate forming ions, etc.). The most effective and technologically convenient among the presently known methods to tackle with scaling is the method of scaling prevention with chemical reagents, scale inhibitors. As scale inhibitors serve organic derivatives of phosphonic and phosphoric acids, nonionogenic phosphates, low-molecular polycarboxylic acids, acid polymers and copolymers, etc. [3]. Upon an appropriate choice of an inhibitor and its appropriate application technology, the deposition of organic salts can be technologically completely precluded along the whole way of well product motion from a hole bottom to oil-and-water processing facilities.

In extraction, transportation, and processing of oil, hydrogen sulfide and mercaptans cause corrosion of the oil-extraction equipment, contaminate the atmosphere, and impair the activity of catalysts to the point of their complete deactivation in oil processing. In 2008, GOST (State Standard) R 51858–2002 came into effect, according to which the maximum content of hydrogen sulfide and mercaptans in oil should not exceed 100 ppm, with this figure to be further reduced to 20 ppm. Hydrogen sulfide neutralizers are used to rapidly and effectively reduce the content of hydrogen sulfide in extracted oil by reacting with hydrogen sulfide to give nonvolatile compounds. An analysis of published data demonstrated that the most widely used hydrogen sulfide and mercaptan neutralizers are those based on formaldehyde and its derivatives are [5–7].

Despite the considerable number of studies in this field, published data on oilfield reagents acting as both scaling inhibitors and hydrogen sulfide neutralizers are nearly lacking at all. It should be noted that the scaling becomes more pronounced in the presence of hydrogen sulfide because of the decreasing solubility of CaCO<sub>3</sub> [8].

The goal of our study was to synthesize from paraformaldehyde, monoethanolamine, and  $P_2O_5$  a new reagent that could simultaneously effectively inhibit the deposition of CaCO<sub>3</sub> and neutralize hydrogen sulfide.

## EXPERIMENTAL

NMR spectra were recorded with a Bruker AM-300 spectrometer with working frequencies of 300.13 (<sup>1</sup>H) and 75.47 MHz (<sup>13</sup>C). The chemical shifts in the <sup>1</sup>H spectrum are given relative to the TMS internal standard. IR spectra were recorded with a Shimadzu IR Prestige spectrometer.

Elemental analysis data were obtained on a Euro EA-3000 CHNS analyzer (HEKArech GmbH).

**1,3,5-Tris(2-hydroxyethyl)hexahydrotriazine (I).** To 6.1 g (0.1 mol) of monoethanolamine was added a solution of 3.0 g (0.1 mol in terms of formaldehyde) of paraformaldehyde in 20 mL of methanol and the mixture was agitated for 2 days. The solvent was evaporated, and the residue, distilled to give 6.3 g (86%) of a light yellow viscous fluid. The physicochemical characteristics of compound (I) were in agreement with published data [9].

2-[3,5-Bis(2-hydroxyethyl)-1,3,5-hexahydrotriazinyl-1]ethyl ester of phosphoric acid (II). To 50.0 g (0.228 mol) of hexahydrotriazine (I) was added under vigorous agitation at 0°C 16.14 g (0.114 mol) of  $P_2O_5$ until a homogeneous mass was formed. The resulting mixture was heated to 80°C for 1 h. A 66.0-g (96%) portion of a light yellow viscous fluid was obtained. Found, %: C 36.18, H 7.38, N 14.21. C<sub>9</sub>H<sub>22</sub>N<sub>3</sub>O<sub>6</sub>P. Calculated, %: C 36.12, H 7.41, N 14.04, P, 10.35.

IR spectrum, v, cm<sup>-1</sup>: 978, 1076, 1249, 1355, 1457, 1653, 1675, 2872–2960, 3100–3570 (OH). <sup>1</sup>H NMR spectrum (300 MHz, δ, ppm, CD<sub>3</sub>OD): 2.82 t (4H, NCH<sub>2</sub>C), 2.98 m (4H, NCH<sub>2</sub>N), 3.31 m (2H, NCH<sub>2</sub>C), 3.82 t (2H, CH<sub>2</sub>O), 3.88 (2H, CH<sub>2</sub>OP), 4.14 m (2H, NCH<sub>2</sub>N), 4.70 m (4H, OH).

Single-reactor method for synthesis of 2-[3,5-bis(2-hydroxyethyl)-1,3,5-hexahydrotriazinyl-1]ethyl ester of phosphoric acid (II). To a solution of 3.0 g of paraformaldehyde in 20 mL of methanol was added 6.1 g (0.1 mol) of monoethanolamine and the mixture was boiled with reflux for 3.5 h. The solvent was evaporated and 2.37 g (0.017 mol) of  $P_2O_5$  was added under vigorous agitation. The resulting mixture was heated to 80°C for 1 h, with 9.5 g (95%) of light yellow viscous liquid obtained.

The efficiency of a scaling inhibitor was determined by capillary blocking in pumping of model produced water (MPW) through the capillary without an inhibitor (blank run) and with it. The model produced water containing Ca<sup>2+</sup>, Na<sup>+</sup>, Cl<sup>-</sup>, and CO<sub>3</sub><sup>2-</sup> was pumped at a flow rate of 1 mL min<sup>-1</sup> through a capillary with length of 2.5 mm and inner diameter of 1 mm at a temperature of 90°C, and the dynamics of the pressure drop in the capillary, caused by deposition of CaCO<sub>3</sub>, was recorded.

The inhibition efficiency was found by the formula

$$E = (\Delta p_1 - \Delta p_2) / \Delta p_1,$$

where  $\Delta p_1$  is the pressure drop in the capillary in pumping-through of MPW without a scaling inhibitor (kPa), and  $\Delta p_2$ , that with a scaling inhibitor (kPa).

The efficiency of a reagent as hydrogen sulfide neutralizer in oil and oilfield water was determined by the standard procedure.

#### **RESULTS AND DISCUSSION**

The 1,3,5-hexahydrotriazine fragment interacts with hydrogen sulfide and thereby neutralizes this compound and phosphoric acid derivatives inhibit the crystallization rate. Therefore, it was of interest to develop a method for obtaining phosphorylated 1,3,5-tris(2-hydroxyethyl)-hexahydrotriazine and study its properties as CaCO<sub>3</sub> deposition inhibitor and hydrogen sulfide neutralizer.

1,3,5-Tris(2-hydroxyethyl)hexahydrotriazine (I) was produced via triple cyclic condensation of monoethanolamine with methoxymethanol in methanol in nearly quantitative yield. Under the chosen conditions and at a fivefold molar excess of methanol in terms of formaldehyde, paraformaldehyde is nearly fully converted to methoxymethanol, which favors a selective course



Scheme 1.

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**Fig. 1.** Effect of phosphorylated 1,3,5-tris(2-hydroxyethyl) hexahydrotriazine (II) on the process of CaCO<sub>3</sub> deposition at concentrations of (1) 0, (2) 10, and (3) 20 mg L<sup>-1</sup> at 90°C. ( $\Delta p$ ) Pressure drop and ( $\tau$ ) time.

of the reaction [10]. Heating of hexahydrotriazine (I) with phosphorus(V) oxide at a 2 : 1 molar ratio and temperature of 80°C gives 2-[3,5-bis(2-hydroxyethyl)-1,3,5-hexahydrotriazinyl-1]ethyl ester of phosphoric acid II in 96% yield. The <sup>1</sup>H NMR spectrum of compound II contains, together with the signals of methylene protons of the triazine ring at 2.82 and 4.14 ppm, also a triplet at 3.88 ppm and a broadened singlet at around 4.70 ppm, associated with protons of the POCH<sub>2</sub>- and HO groups. The IR spectrum shows absorption bands at ~978 and ~1249 cm<sup>-1</sup>, characteristic of stretching vibrations of P–O–C phosphoric acid esters [11] (Scheme 1).

Of particular interest are methods for synthesis of the compounds without production and isolation of intermediate substances. In this context, we developed a single-reactor double-stage method for obtaining phosphoric acid ester **II**: methoxymethanol was boiled



**Fig. 2.** Efficiency *E* of hydrogen sulfide neutralization with phosphorylated 1,3,5-tris(2-hydroxyethyl)hexahydrotriazine (II) vs. the interaction duration  $\tau$  at reagent : hydrogen sulfide molar ratios of (1) 9 : 1 and (2) 6 : 1.

with monoethanolamine for 3.5 h and  $P_2O_5$  was added to the resulting reaction mass to give phosphorylated 1,3,5-tris(2-hydroxyethyl)hexahydrotriazine (II) the purity of which is about 95% according to <sup>1</sup>H NMR data.

A study of phosphorylated 1,3,5-tris(2-hydroxyethyl)hexahydrotriazine (II) demonstrated that this compound has properties of both a scaling inhibitor and a hydrogen sulfide neutralizer. At concentrations of 10 and 20 mg L<sup>-1</sup>, the reagent nearly fully inhibits the process of CaCO<sub>3</sub> deposition, with its efficiency being about 98% (Fig. 1).

The reagent was tested by the standard procedure for determining the efficiency of hydrogen sulfide absorption. It can be seen in the table that even at a so small consumption coefficient of reagent **II**, the efficiency of hydrogen sulfide absorption by the neutralizer exceeds 95%. Figure 2 shows the dependence of the neutraliza-

H <sub>2</sub> S-Containing liquid	Consumption coefficient K, mg mg <sup>-1</sup> 2S	$H_2S$ concentration, mg $L^{-1}$		
		before absorption	after absorption	Efficiency, %
Sorochinsk oil	3	1932	579.6	70
Sorochinsk oil	3	1700	221	87
Sorochinsk water	3	260	Trace amounts	99

Efficiency of hydrogen sulfide neutralization by reagent II

tion efficiency on the exposure duration, whence follows that the efficiency of reagent **II** does not decrease in the course of time.

Reagent II is compatible with mineralized stratal water of the following composition (g L<sup>-1</sup>): NaCl 91.37, CaCl<sub>2</sub> 10.21, MgCl<sub>2</sub> 36.74, NaHCO<sub>3</sub> 0.42, Na<sub>2</sub>SO<sub>4</sub> 0.187, H<sub>2</sub>S 187 mg L<sup>-1</sup> (Salyuka booster pump station, RN-Severnaya neft') and NaCl 72.72, CaCl<sub>2</sub> 9.71, MgCl<sub>2</sub> 16.44, NaHCO<sub>3</sub> 0.378, Na<sub>2</sub>SO<sub>4</sub> 0.36, H<sub>2</sub>S 144 mg L<sup>-1</sup> (Sandiveu booster pump station, RN-Severnaya neft'). No precipitates are formed during three days.

The resulting 2-[3,5-bis(2-hydroxyethyl)-1,3,5hexahydrotriazinyl-1]ethyl ester of phosphoric acid (II) is effective for scaling inhibition and serpentines neutralization and can find use as a reagent in development of oil-and-gas fields.

### CONCLUSIONS

A method for producing from 1,3,5-tris(2-hydroxyethyl)hexahydrotriazine and phosphorus(V) oxide a new integrated oilfield reagent that is compatible with stratal water and is effective both for scaling inhibition and hydrogen sulfide neutralization.

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