Performance of waterborne polyurethane based on N-tert-butyldiethanolamine in corrosion inhibition

Y Zaripova1,*, M Varfolomeev1, R Pavelyev1, A Farhadian2, V Yarkovoi3, S Vinogradova4 and I Vakhitov1
1 Kazan Federal University, Russia
2 Shahid Beheshti University, Iran
3 Gazprom VNIIGAZ, Russia
4 Kazan National Research Technological University, Russia

Abstract. The design of bifunctional inhibitors effectively preventing hydrate formation and corrosion is a relevant issue for the oil and gas industry. In this work, we expanded the study of the corrosion inhibition effectiveness for waterborne polyurethanes (WPUs) obtained earlier and shown to be promising inhibitors. The corrosion inhibition ability of WPUs was assessed using weight-loss and electrochemical methods. Commercial corrosion inhibitor Armohib CI-28 was taken as a reference sample. The data obtained showed that the tert-Bu-WPU sample is able to effectively inhibit acid and carbon dioxide corrosion at room temperature; however, with an increase in temperature, its efficiency decreases more intensively than for a commercial inhibitor. In general, waterborne polyurethanes are promising alternatives to commercial reagents due to their multifunctionality.

1. Introduction
The challenges facing the oil and gas industry today include hydrate formation and corrosion. Gas hydrates are crystalline ice-like compounds in which a gas molecule is enclosed in a cell of water molecules [1]. They are formed at low temperatures and high pressures, which is often realized in fields located in the northern regions. The formation of hydrates is facilitated by the high flow rate and the presence of crystallization centers (for example, welds, sand). In transport pipelines, this process can cause partial or complete blockage of the hydrocarbon flow, which in turn can lead to economic losses and environmental pollution [2]. Methods to combat this process include physical methods (pressure reduction, heating) and chemical methods (injection of inhibitors). Inhibitors of hydrate formation are divided into thermodynamic (THIs), kinetic (KHIIs) and anti-agglomerants (AAs) [3]. THIs shift the equilibrium conditions of hydrate formation towards lower temperatures and higher pressures; such inhibitors require large amounts, high concentrations, most of them are quite toxic compounds (methanol, ethylene glycol). KHIIs and AAs belong to the so-called low-dose inhibitors and are increasingly replacing thermodynamic ones. What about the action mechanism, kinetic inhibitors (vinyl lactam-based polymers, poly(N-alkylacrylamide)s, ionic liquids, amino acids, proteins [4-6]) increase the time of induction of hydrate formation, and anti-agglomerants (phosphonium and quaternary ammonium compounds [4]) allow nucleation, but prevent further growth of hydrate crystals, and thus the hydrate in the form of a suspension moves along with the fluid flow.
Corrosion is another major economic problem in the oil and gas industry. Carbon steel is widely used material due to its good mechanical properties and reasonable price [7]. However, carbon steel is highly susceptible to corrosion in aggressive environments (oxygen, hydrochloric acid, acidic gases (CO2, H2S) [8]). To combat corrosion, alloying, cathodic and anodic protection and the introduction of corrosion inhibitors (CIs) are used, which is a relatively profitable and effective method. CIs can be classified as neutralizing, scavenging, and film-forming according to their inhibition mechanism. Imidazolines, quaternary ammonium surfactants and phosphate esters are the most common flow line CIs [8].

Of course, in addition to the listed problems, there are also the precipitation of paraffins, asphaltenes, scale deposition and much more. All these aspects require a large number of different reagents. Consequently, difficulties arise such as high cost, infrastructure for delivery and storage, regeneration, increased environmental impact, as well as the problem of compatibility, because it was shown that in some cases inhibitors of different types can suppress each other’s action with simultaneous injection [9,10]. In this regard, there is such a challenge as the creation of a multifunctional biodegradable oilfield reagent. In this case, the following requirements are imposed on the reagent: good solubility in water; effectiveness at low concentrations; the presence of hydrocarbon fragments (alkyl, aromatic) to disrupt the structure of water and create a distance between its molecules; the presence of centers that can be adsorbed on the metal surface; from an environmental point of view, they must be non-toxic and biodegradable; from an economic point of view - cheap.

Earlier, a new class of hydrate inhibitors based on waterborne polyurethanes was developed [11-13]. These compounds performed well in comparison with commercial reagents such as PVP and PVCap. In the present work, the ability of inhibitors based on polyurethanes to prevent corrosion was assessed by the methods of gravimetry and electrochemistry.

2. Materials and methods

2.1. Materials
All reagents were obtained from commercial sources and were used without further purification. Deionized water prepared by Arium mini plus ultra-pure water system (Sartorius, Germany) to achieve resistivity 18.20 MΩ·cm at 25 °C was used in all experiments. Commercial corrosion inhibitor Armohib CI-28 (AkzoNobel, Netherlands) was used for comparison.

2.2. Preparation of waterborne polyurethanes
Waterborne polyurethanes for the study of anticorrosive activity were obtained according to the methods described in [11,14].

2.3. Corrosion weight-loss experiments
Carbon steel (CS) coupons with dimensions of 2.54 × 5.08 cm and composition of (wt%) C, 0.24; Si, 0.37; Mn, 0.65; Cu, 0.25; Ni, 0.25; As, 0.08; S, 0.045; P, 0.035 and Fe, 98.08 were washed 5 times with water and ethanol. Emery papers (800, 1000, and 1200 grades) were used to polish the surface of CS followed by its rewashing with distilled water and ethanol. The high-resolution analytical balance (0.00001 g) was employed for weighing the initial (W₀) and final (W₂₄) masses of CS. Experiments were performed in the acid solution (2M HCl) at different concentrations of inhibitor for 24 h in open glass
vials at 25, 50 and 75 °C. Before the re-weighing, the steel coupons were washed three times with ethanol and distilled water. The experiment was repeated three times to ensure repeatability of results. The corrosion rate (mm/y), inhibition efficiency (%IEw), and surface coverage (θ) were calculated using the following equations [15]:

\[ CR = \frac{8.76 \times 10^4 \times \Delta m}{s \times t \times \rho} \]  \hspace{1cm} (1)

\[ \%IEw = \frac{CR_0 - CR_{inh}}{CR_0} \times 100\% \]  \hspace{1cm} (2)

\[ \theta = \frac{CR_0 - CR_{inh}}{CR_0} \]  \hspace{1cm} (3)

where \( \Delta m \) (g), \( s \) (cm\(^2\)), \( t \) (h), and \( \rho \) (g cm\(^{-3}\)) are the average value of the weight loss of CS, the total area of the CS, the corrosion time and the density of the CS, respectively.

2.4. Electrochemical measurements

The same carbon steel coupons (CS) and their preparation procedure (washing and polishing) were used. The tests were conducted in the electrochemical three-electrode cell in static mode under the natural aeration at different temperatures °C in 2M HCl solution, with and without an inhibitor. The whole experiment was carried out in deionized water. The surface area of the working electrode was 10 cm\(^2\) (50 × 25 × 1 cm) with the waterline isolated by varnish. The main reference electrode was EVL-IM3 type silver chloride one. The auxiliary reference electrode was made of the same material as the working one; the auxiliary one was a platinum electrode. Before testing procedures, a sample’s surface was cleaned off grease by soda, distilled water, and ethanol followed by drying at room temperature.

Electrochemical measurements were carried out by ZIVE SP2 workstation. After immersion of samples in solution, the values of open-circuit potential (EOCP) were acquired at least for one hour. If the potential value variation did not exceed 30 mV over the last 0.5 h, the value of the potential at the end of immersion was taken as EOCP. Potentiodynamic polarization was carried out by sweeping the working electrode potential ±250 mV away from the EOCP at 1 mV s\(^{-1}\) scan rate. Anodic and cathodic polarization curves showing the correlation between the potential of the studied electrode and the current density upon polarization from an external direct current source were registered. Then the kinetic parameters of reaction were determined, namely corrosion potential and current, the values of Tafel equation parameters (Tafel slopes), and corrosion rate as well. To determine the corrosion resistance the linear polarization curves were recorded by sweeping the working electrode potential ±20 mV away from the EOCP at 0.5 mV s\(^{-1}\) scan rate. The corrosion current density (\( I_{corr} \)) and \( E_{corr} \) were obtained by extrapolation of the Tafel lines. The inhibition efficiency (\%IE) was computed as follows:

\[ \%IE = (1 - \frac{I_{corr}}{I_{corr}^0}) \times 100\% \]  \hspace{1cm} (4)

where \( I_{corr}^0 \) is the corrosion current density for blank system (2M HCl solution) and \( I_{corr} \) is the corrosion current density with an inhibitor.

3. Results and discussion

3.1. Salt solution corrosion

An electrochemical method was used to study the inhibitory effect of one of the first presented water-soluble polyurethanes, which showed good anti-hydrate activity [11]. The assessment of the ability to prevent corrosion was carried out using a model of brine formation water with a density of 1.12 g/cm\(^3\). The measurements were taken at 25 °C without stirring. Figures 2 and 3 show the open circuit potential and potentiodynamic polarization curves, respectively. Data on potentials (\( E_{corr} \)) and corrosion currents (\( I_{corr} \)), slopes of the Tafel sections of polarization curves (\( \beta_a, \beta_c \)) after the introduction of a corrosion inhibitor into the solution are given in Table 1.
**Figure 2.** Open-circuit potential values for a corrosion inhibitor in solutions of various concentrations (trend lines).

**Figure 3.** Potentiodynamic polarization curves for a carbon steel electrode in 2M HCl without and with various inhibitor concentrations.
Table 1. Kinetic parameters for the test steel in the presence of inhibitor of various concentrations.

| Inhibitor concentration | $E_{o,c,p}$ (mV SCE) | $\beta_a$ (V/div) | $\beta_c$ (V/div) | $E_{corr}$ (mV) | $I_{corr}$ (mA/cm$^2$) | $R_p$ (mΩ) | %IE  |
|-------------------------|----------------------|-------------------|-------------------|-----------------|------------------------|-----------|------|
| 1000 ppm                | -437                 | 0.070             | 0.096             | -420.040        | 0.012                  | 161.804   | 90.7 |
| 500 ppm                 | -449                 | 0.078             | 0.106             | -433.274        | 0.026                  | 76.286    | 79.8 |
| 100 ppm                 | -468                 | 0.068             | 0.147             | -408.760        | 0.055                  | 31.873    | 57.2 |
| 50 ppm                  | -471                 | 0.047             | 0.172             | -358.461        | 0.082                  | 19.632    | 36.2 |
| 0 ppm                   | -511                 | 0.054             | 0.080             | -482.008        | 0.129                  | 10.860    |      |

The introduction of inhibitor leads to a decrease in the rate of oxidative and reduction reactions, as evidenced by the value of the inhibition coefficient 36.2 - 90.7%.

The shift of the corrosion potential to the positive region from -0.51V to -0.43V for this inhibitor indicates that positively charged inhibitor molecules are adsorbed on the electrode surface and the inhibitory effect is associated with an increase in the overvoltage of electrode reactions.

The introduction of inhibitor also affects the limiting stages of reactions (dissolution of anodic carbon steel and cathodic reactions of hydrogen evolution), which manifests itself in a change in the slopes of the curves in the region of anodic polarization. The change in the slopes of the curves in the region of cathodic and anodic polarization is insignificant, which indicates that this compound can be classified as a mixed type inhibitor.

3.2. HCl corrosion

After the first success of waterborne polyurethanes in inhibiting hydrate formation, systematic studies began to identify the dependence of the inhibitory properties of these polymers on their structure. A number of polyurethanes with various diethanolamine fragments were synthesized, some of which exhibited the properties of bifunctional inhibitors preventing hydrate formation, as well as acid corrosion at a temperature of 25 °C [14].

3.2.1. Weight-loss experiments. Sample tert-Bu-WPU in weight-loss experiments showed an inhibition efficiency of 90.6% at a concentration of 100 ppm [14]. It was decided to test whether this compound would work effectively at higher temperatures. Below are the results of gravimetric studies at 50 and 75 °C.

Table 2. Corrosion rate data in the presence of inhibitors at different temperatures (gravimetry).

| Sample        | Concentration | Corrosion rate (mm/year) | %IE  |
|---------------|---------------|--------------------------|------|
| 25 °C         |               |                          |      |
| W/o inhibitor | -             | 9.19                     | -    |
| tert-Bu-WPU   | 100 ppm       | 0.41                     | 90.6 |
| Armohib CI-28 | 100 ppm       | 0.058                    | 98.7 |
| 50 °C         |               |                          |      |
| W/o inhibitor | -             | 73.74                    | -    |
| tert-Bu-WPU   | 100 ppm       | 38.00                    | 48.5 |
| Armohib CI-28 | 100 ppm       | 1.09                     | 98.5 |
| 75 °C         |               |                          |      |
| W/o inhibitor | -             | 78.06                    | -    |
| tert-Bu-WPU   | 100 ppm       | 74.07                    | 5.1  |
| Armohib CI-28 | 100 ppm       | 27.84                    | 64.3 |
It can be seen (Table 2) that if at 25 °C both the commercial inhibitor and the inhibitor based on polyurethane effectively prevent corrosion, then already at 50 °C tert-Bu-WPU sample significantly loses its properties. At a temperature of 75 °C, the effect of Armohib CI-28 is also reduced. In addition, to visualize the effect of inhibitors, plates corroded at different temperatures were examined using profilometry.

![Figure 4. Surface topography of steel coupons.](image)

Surface images clearly illustrate the decrease in corrosion inhibition efficiency with increasing temperature. In general, it can be concluded that at a temperature close to room temperature, the effectiveness of inhibitors is maximum.

### 3.2.2. Electrochemical measurements.

The electrochemical study of corrosion inhibition was also supplemented with data at different temperatures.
**Table 3.** Kinetic parameters of corrosion of steel plates in the presence of tert-Bu-WPU inhibitor at different temperatures.

| Inhibitor concentration | $E_{ocp}$ (mV SCE) | $\beta_a$ (V/div) | $\beta_c$ (V/div) | $E_{corr}$ (mV) | $I_{corr}$ (mA cm$^{-2}$) | $R_p$ (m$\Omega$) | %IE |
|-------------------------|--------------------|--------------------|--------------------|----------------|--------------------------|----------------|-----|
| **25 °C w/o stirring**  |                    |                    |                    |                |                          |                |     |
| 500 ppm                 | -460.8             | 0.090              | 0.205              | -459.099       | 0.1024                   | 11.42          | 70.5|
| 100 ppm                 | -462.6             | 0.138              | 0.179              | -497.252       | 0.1473                   | 9.52           | 57.5|
| 50 ppm                  | -464.2             | 0.090              | 0.154              | -486.421       | 0.1668                   | 12.91          | 51.9|
| 0 ppm                   | -511.5             | 0.118              | 0.192              | -504.618       | 0.3467                   | 9.12           | -   |
| **25 °C with stirring**  |                    |                    |                    |                |                          |                |     |
| 500 ppm                 | -496.8             | 0.067              | 0.139              | -486.537       | 0.064                    | 30.673         | 50.7|
| 100 ppm                 | -499.9             | 0.075              | 0.188              | -481.106       | 0.095                    | 24.540         | 27.1|
| 50 ppm                  | -492.9             | 0.079              | 0.231              | -478.309       | 0.104                    | 24.676         | 19.7|
| **50 °C w/o stirring**  |                    |                    |                    |                |                          |                |     |
| 500 ppm                 | -517.6             | 0.078              | 0.153              | -509.5         | 0.247                    | 9.105          | 81.0|
| 100 ppm                 | -522.2             | 0.08               | 0.151              | -514.6         | 0.219                    | 10.358         | 83.2|
| 50 ppm                  | -508.1             | 0.063              | 0.083              | -517.064       | 0.282                    | 5.537          | 74.4|
| 0 ppm                   | -536.2             | 0.071              | 0.135              | -505.7         | 1.3                      | 1.511          | -   |
| **75 °C w/o stirring**  |                    |                    |                    |                |                          |                |     |
| 500 ppm                 | -513.3             | 0.097              | 0.254              | -494.281       | 1.3                      | 2.54           | 49.6|
| 100 ppm                 | -518.2             | 0.056              | 0.094              | -502.227       | 1.70                     | 0.889          | 33.9|
| 50 ppm                  | -523.4             | 0.062              | 0.088              | -498.754       | 1.86                     | 0.848          | 27.7|
| 0 ppm                   | -519.7             | 0.062              | 0.093              | -511.388       | 2.6                      | 0.630          | -   |

Table 3 shows the kinetic parameters of corrosion of steel plates in the presence of tert-Bu-WPU inhibitor at different temperatures under static and dynamic (stirring) conditions. As can be seen from this table, under dynamic conditions, the efficiency of inhibition of acid corrosion at a concentration of 500 ppm drops significantly from 71% without stirring to 51% with stirring, which is associated with the difficulty of binding the polymer to the steel surface. With an increase in temperature, a dome-shaped dependence is observed for the polymer under study - at 50 °C, inhibition improves to 81% and again deteriorates to 50% at 75 °C.

### 3.3. CO₂ corrosion

One of the most common types of corrosion in fields is carbon dioxide corrosion. The study of CO₂ corrosion for tert-Bu-WPU was carried out according to the «bubble test» method, carbon dioxide was passed through the solution to saturate CO₂ and remove oxygen. The cell was a glass vessel with a volume of 0.5 liters, closed with a fluoroplastic lid. A working electrode, a reference electrode, an auxiliary electrode, and a glass tube with a ceramic atomizer for supplying carbon dioxide were introduced into the cell through the lid. The cell was closed with a lid and CO₂ was purged for 10-15
minutes at a volumetric flow rate of 30 ml/min. Then, the solution was poured into the cell, and CO2
was blown at the same volumetric flow rate for 20-30 min. After that, the volumetric flow rate of CO2
was reduced to 5-8 ml/min, and electrodes were inserted for research at room temperature. The solution
was a model of saline formation water with a density of 1.12 g/cm³.

The open circuit potential values for tert-Bu-WPU solution at 50 ppm and 100 ppm concentrations
are shown in Figure 5. Potentiodynamic polarization curves (Tafel curves) for a carbon steel electrode
with the same concentrations of tert-Bu-WPU inhibitor are shown in Figure 6. Kinetic parameters for
the investigated steels in the presence of tert-Bu-WPU inhibitor are shown in Table 4.

**Figure 5.** Open-circuit potential values for tert-Bu-WPU corrosion inhibitor in solutions
of various concentrations (trend lines).

**Figure 6.** Potentiodynamic polarization curves (Tafel curves) for a carbon steel electrode with
different concentrations of tert-Bu-WPU inhibitor with stirring.
Table 4. Kinetic parameters for the test steel in the presence of tert-Bu-WPU inhibitor of various concentrations.

| Inhibitor concentration (ppm) | $E_{ocp}$ (mV SCE) | $\beta_a$ (V/div) | $\beta_c$ (V/div) | $E_{corr}$ (mV) | $I_{corr}$ (mA/cm$^2$) | $R_p$ (mΩ) | %IE |
|-----------------------------|-------------------|-------------------|-------------------|-----------------|-----------------------|-----------|------|
| 100                         | -569              | 0.064             | 0.129             | -583.2          | 0.001                 | 1.44k     | 87.5 |
| 50                          | -582              | 0.062             | 0.257             | -644.53         | 0.002                 | 942.2     | 75   |
| 0                           | -611              | 0.053             | 0.144             | -699.1          | 0.008                 | 276.955   | -    |

As can be seen from the presented materials, this inhibitor is much more effective under conditions of carbon dioxide corrosion than under conditions of acid corrosion. So, at a concentration of 100 ppm, the inhibition of carbon dioxide corrosion is 88% versus 58% for acid corrosion. There is a direct dependence of the efficiency of corrosion inhibition on the concentration of the inhibitor.

4. Conclusion

Using electrochemical methods and gravimetry, the ability of waterborne polyurethanes, obtained by our research team earlier and showed excellent activity in inhibiting hydrate formation, to inhibit corrosion of carbon steel in a model of brine formation water, as well as in a solution of hydrochloric acid and when passing carbon dioxide, was studied. Previous research was expanded by conducting experiments at elevated temperatures. In the case of hydrochloric acid, the corrosion inhibition efficiency for tert-Bu-WPU has been shown to be about 90% at a concentration of 100 ppm at 25 °C. With an increase in temperature, the efficiency naturally decreases to about 50% at 50 °C and almost completely disappears at 75 °C (5%). At the same time, the commercial corrosion inhibitor Armohib CI-28 loses its effectiveness up to 64% only at a temperature of 75 °C, at temperatures of 25 °C and 50 °C its effectiveness remains at the level of 98% at a concentration of 100 ppm. It can be assumed that when tert-Bu-WPU is used at concentrations above 0.1 wt% (1000 ppm), that is, as kinetic inhibitors of hydrate formation, they will necessarily exhibit good anticorrosive properties. Also, the presented sample is capable of inhibiting carbon dioxide corrosion. In general, it should be noted that this class of hydrate inhibitors is promising from the point of view of the development of multifunctional petrochemical reagents, since it is relatively easy to impart the desired properties to polyurethanes of this kind by using the corresponding monomers in the synthesis.

Acknowledgements

The reported study was funded by RFBR and The Research Council of Norway according to the research project № 20-55-20010.

References

[1] Sloan E D 2003 Fundamental principles and applications of natural gas hydrates, *Nature* **426**, 353.
[2] Hassanpouryouzband A, Joonaki E, Farahani M V, et al. 2020 Gas hydrates in sustainable chemistry, *Chem. Soc. Rev.* **49**, 5225–309.
[3] Sloan E D, Koh C A, Sum A K, et al. 2011 *Natural Gas Hydrates in Flow Assurance* (Elsevier Inc.).
[4] Perrin A, Musa O M, Steed J W 2013 The chemistry of low dosage clathrate hydrate inhibitors, *Chem. Soc. Rev.* **42** (5), 1996–2015.
[5] Tariq M, Rooney D, Othman E, Aparicio S, Atihlan M, Khraisheh M 2014 Gas hydrate inhibition: A review of the role of ionic liquids, *Ind. Eng. Chem. Res.* **53** (46), 17855–68.
[6] Kelland M A 2018 A review of kinetic hydrate inhibitors from an environmental perspective, *Energy Fuels* **32**, 12001–12.
[7] Lei X, Wang H, Mao F, et al. 2018 Electrochemical behaviour of martensitic stainless steel after immersion in a H$_2$S-Saturated solution, *Corros. Sci.* **131**, 164–73.
[8] Reynolds M A 2020 A Technical playbook for chemicals and additives used in the hydraulic fracturing
of shales, *Energy Fuels* **34**, 15106–25.

[9] Moore J, Ver Vers L, Conrad P 2009 Understanding kinetic hydrate inhibitor and corrosion inhibitor interactions, *Proc. of the Offshore Technology Conf.* (Houston, TX, USA: May 4 – 7, 2009) **1**, 477-81.

[10] Qasim A, Khan M S, Lal B, Shari A M 2019 A perspective on dual purpose gas hydrate and corrosion inhibitors for flow assurance, *J. Pet. Sci. Eng.* **183**, 106418.

[11] Farhadian A, Kudbanov A, Varfolomeev M A, Dalmazzone D 2019 Waterborne polyurethanes as a new and promising class of kinetic inhibitors for methane hydrate formation, *Sci. Rep.* **9**, 9797.

[12] Farhadian A, Varfolomeev M A, Kudbanov A, Rezaeisadat M, Nurgaliev D K 2020 Waterborne polymers as kinetic/anti-agglomerant methane hydrate and corrosion inhibitors: A new and promising strategy for flow assurance, *J. Nat. Gas Sci. Eng.* **77**, 103235.

[13] Farhadian A, Varfolomeev M A, Kudbanov A, Gallyamova S R 2019 A new class of promising biodegradable kinetic/anti-agglomerant methane hydrate inhibitors based on castor oil, *Chem. Eng. Sci.* **206**, 507–17.

[14] Pavelyev R S, Zaripova Y F, Yarkovoi V V, et al. 2020 Performance of waterborne polyurethanes in inhibition of gas hydrate formation and corrosion: Influence of hydrophobic fragments, *Molecules* **25**, 5664.

[15] Cui G, Guo J, Zhang Y, et al. 2019 Chitosan oligosaccharide derivatives as green corrosion inhibitors for P110 steel in a carbon-dioxidesaturated chloride solution, *Carbohydr. Polym.* **203**, 386–95.