Cyclic Potentiometric Polarization and Resistance of Mild Steel in an Environment of Alcohols and Their Blends with Gasoline

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ABSTRACT: Nowadays, there is an effort to increase the more widespread use of biofuels that are a renewable energy source in transportation and an alternative to conventional, petroleum-based fuels. These biofuels include alcohols such as biomethanol, bioethanol, and biobutanol that have a high octane number, but generally different physical and chemical properties than petroleum fuels. The different properties of alcohols may cause low material compatibility with carbon steel. Here, we used cyclic potentiodynamic polarization (CPP) to study the behavior of carbon steel in an environment of alcohols and alcohol–gasoline blends (AGBs). Using CPP, we proved that the corrosion of mild steel can be significantly influenced by alcohol properties, such as the chain length, pKa, and solubility of oxygen and water. In the environment of pure alcohols (not blended by gasoline), a very good passivation ability of steel was proven, especially for n-butanol. In AGBs, steel corrosion can also be influenced by the gasoline amount. When these pure alcohols or their gasoline blends are contaminated by water-containing chlorides and organic acids, the corrosion rate of carbon steel can increase by up to 4 orders of magnitude. In an anhydrous environment of alcohols, the CPP can give results with a very good informative value.

1. INTRODUCTION

The increasing global energy demands, limited world fossil fuel reserves, and efforts to improve air quality have led society to look for alternative energy sources that could partially replace fossil sources and contribute to reducing the greenhouse gas emissions. Biofuels produced from biomass are one of the alternatives to conventional petroleum-based fuels. Biomethanol, bioethanol, and biobutanol with high octane numbers are a suitable variant of biofuels for petrol engines.

Biomethanol can be produced from synthesis gas obtained by biomass gasification. However, this option is not widely represented thus far as its production from the biomass is roughly twice as expensive as that from natural gas.1 Biomethanol can either be used as a pure M100 fuel or as mixed M85 or M15 fuels. The high oxygen content and the associated low-energy content, high material incompatibility, and the formation of azeotropes with hydrocarbons are the main disadvantages of biomethanol.1

Bioethanol is most widely used especially in Brazil, where nearly 20% of cars burn pure ethanol (E100 azetropo), while the rest of the car fleet is adapted to use E22 and E85 fuels.2,3 Ethanol–gasoline blends (EGBs) are widely used in the US and the EU as well, mostly in the form of E10 and E85 fuels. In the Czech Republic, gasolines with an ethanol content of up to 5 vol % and E85 fuels are being used, and the implementation of E10 fuels from 2019 is being considered. The use of (bio)ethanol as a transportation fuel is associated with a number of technical problems.4−7 Because of the application of EGBs in transportation, high demands are placed on their quality and material compatibility. The increased corrosion aggressiveness of EGBs and alcohol–gasoline blends (AGBs), in general, is given by the ability of alcohols to increase the conductivity and water solubility in these blends.4,8−10 Acidic substances, which may result from the oxidation of some unsaturated hydrocarbons gasolines, may significantly increase the aggressiveness of AGBs also.10 Furthermore, chlorides that may come from the alcohol production or secondary contamination may have a major impact on the aggressiveness of AGBs as well.7 The corrosive effects mainly show up on the metal components of the fuel systems and internal engine components, such as the fuel tanks or cylinder walls.3

Biobutanol is another prospective biocomponent potentially applicable in AGBs.11 Biobutanol has about a 31% higher energy content than ethanol and it can be added into gasolines in the amounts of up to 10 vol % so that the criteria for the upper limit for the oxygen content (2.7 wt %) set by the EN 228 standard are still met.12 In comparison with conventional petroleum-based gasolines and EGBs, biobutanol and bio-
butanol-based fuels are safer as they evaporate less at higher temperatures.\textsuperscript{11} Butanol absorbs less water than ethanol and is, thus, less corrosive. Like ethanol, butanol biodegrades well and does not represent an environmental burden-like conventional gasolines.\textsuperscript{13}

A number of publications deal with the corrosion properties of AGBs, especially those with methanol\textsuperscript{14–17} or ethanol\textsuperscript{10,17–25} as an alcohol component. There are several methods applicable for corrosion studies. These methods can be divided into gravimetric\textsuperscript{26,27} and electrochemical\textsuperscript{9,10,14–16,25} methods. The gravimetric methods typically have low demands on experimental equipment, but they are typically time-consuming. Conversely, electrochemical methods typically have higher demands on experimental equipment, but they are time-efficient and can provide more information about the ongoing corrosion processes.\textsuperscript{27} Open-circuit potential (OCP) measurements,\textsuperscript{14,20,21} electrochemical impedance spectroscopy (EIS),\textsuperscript{9,15,18,19} or polarization characteristics measurements,\textsuperscript{15,22} such as cyclic potentiodynamic polarization (CPP),\textsuperscript{17,19,20,22} are examples of the electrochemical methods applicable for the corrosion studies of AGBs. Several studies have been carried out to describe the effects of chlorides, water, pH, and the dissolved oxygen content in ethanol and EGBs on the corrosion of low-alloy steel and aluminum alloys using CPP in a three-electrode arrangement.\textsuperscript{14–22} This work deals with the use of potentiodynamic polarization to study the mild steel corrosion in an environment of different alcohols (methanol, ethanol, isopropanol, n-butanol), and AGBs. Also, the effect of the contamination of these environments with water, chlorides, and acetic acid was studied.

An overview of the basic chemical—physical properties of methanol, ethanol, isopropanol, and n-butanol, which have a major influence on their aggressiveness, is compared in Table 1.

2. RESULTS AND DISCUSSION

2.1. Stabilization of the Corrosion Potential of an Open Circuit. Figure 1 illustrates the selected records of the OCP stabilization for 1 h. From the records of the OCP in the environments of the pure methanol, pure ethanol, and ethanol containing a 6 vol % of water, the potential increase in time is obvious but without any higher fluctuations that could indicate the potential corrosion of mild steel. This OCP increase in time is associated with the consumption of the dissolved oxygen in the environment, where the formation of oxides in the form of a film on the mild steel surface occurs, and the surface is, thus, partially protected against further corrosion. This phenomenon does not occur in the methanol containing a 6 vol % of water. Thus, it is likely that, in this environment, the corrosion resistance of the mild steel will be the lowest and consequently, the susceptibility of the mild steel to corrosion will be the highest. This conclusion is supported by the OCP curve, for which a slight potential decrease can be observed; the corrosion potential is rapidly stabilized at its lowest value and the OCP is not as smooth as in the previous cases. It can be assumed that with an increasing water content, the OCP record would further decrease. This phenomenon may be caused by the occurrence of surface and pitting corrosion due to the presence of chlorides. The lowest potentials, in both methanol and ethanol, were measured after their contamination. For methanol, the influence of water on the change in the environment aggressiveness was significantly higher than for ethanol. The presence of water plays an essential role in the change of the solvent structure and its physical and chemical properties such as the dielectric constant, oxygen content, and proton activity. Shchukarev and Tolmacheva,\textsuperscript{29} who studied ethanol—water environments, report that the concentration of the dissolved oxygen decreased with the increasing water content in the ethanol—water environments. The combination of all these effects, caused by the presence of the water in the ethanol (but in the methanol also), leads to a significant change in the reaction rates of the total corrosion and the passivation mechanism.

2.2. Electrochemical Impedance Spectroscopy. As a result of the relatively high polarity of alcohols which do not exhibit high environmental resistance and have sufficient conductivity, all of the measured impedance spectra had, in the complex plane, the form of two relatively well-separated half circles centered below the real axis. Thus, the spectra consisted of high- and low-frequency parts; see Figure 2. The high-frequency part corresponds to the impedance response (the so-called spatial impedance) that is associated with the environment properties such as resistivity and relative permittivity. The low-frequency part is related to the response of the electric double layer at the phase interface and the polarization

![](image-url)
As oxidation products during the long-term storage of AGBs.\textsuperscript{10}

The evaluation was performed by the approximation of the low-frequency experimental data of the impedance spectra using an equivalent circuit consisting of a series of polarization resistance of the environment \(R_e\) and a parallelly connected polarization resistance \(R_p\) with a constant phase element (CPE). The impedance of this circuit can be expressed using eq 1.

\[
Z = R_e + \frac{R_p}{1 + R_p Q^{-1} (j \omega)^n}\]

Q is a CPE coefficient, \(n\) is a CPE exponent, \(\omega\) is the angular frequency, and \(j\) is an imaginary unit. All of the evaluated data are presented in Table 2.

From Table 2, it is obvious that the resistivity of the alcohols \(R_e\) was increasing with the increasing carbon number in the molecule of the alcohols. This resistivity decrease in a series is in accordance with the decreasing relative permittivity of alcohols that act less as a dielectric with an increasing carbon number in the molecule; see Table 1. The increase in the resistivity was significantly influenced by the addition of the gasoline that has very low permittivity (see Table 1) and very high resistivity (in the order of G\(\Omega\)·cm).\textsuperscript{9,10} On the contrary, the contamination of the alcohols and AGBs by an aqueous solution of acids and salts resulted in a significant resistivity decrease. Water, salts, and acids are generally problematic in biofuel blends and can cause high financial losses for the production, transport, and storage facilities.\textsuperscript{7} Water and salts can come as primary or secondary contaminants either from the alcohol production or they can result from a violation of good transportation and storage practices. Acids can be formed as oxidation products during the long-term storage of AGBs.\textsuperscript{10}

Figure 2. Impedance spectra of the mild steel measured in the environments of the M60 and E60 fuels; the equivalent circuit used to evaluate the low-frequency spectra parts is shown inside the figure: \(R_{\text{fuel}}\) is the environmental resistance, \(R_p\) is the polarization resistance, and \(CPE_{dl}\) is the CPE related to the loss capacitance of the electric double layer.

| Environment | \(R_e\) (k\(\Omega\)·cm\(^{-1}\)) | \(Q\) (\(\Omega\)\(^{-1}\)·s\(^{-1}\))·cm\(^{-2}\)) | \(n\) | \(R_{\text{dl}}\) (k\(\Omega\)·cm\(^{-1}\)) |
|-------------|-------------------|-----------------|-----|-------------------|
| M100        | 24                | 13.3            | 0.700 | 499               |
| M80         | 35                | 9.12            | 0.598 | 747               |
| M60         | 46                | 11.2            | 0.696 | 442               |
| E100        | 91                | 7.28            | 0.817 | 610               |
| E80         | 183               | 7.66            | 0.642 | 430               |
| E60         | 209               | 7.82            | 0.655 | 1293              |
| iP100       | 334               | 4.49            | 0.591 | 839               |
| iP80        | 453               | 4.75            | 0.658 | 1534              |
| iP60        | 492               | 4.98            | 0.632 | 1128              |
| B100        | 308               | 5.12            | 0.673 | 1467              |
| B80         | 510               | 5.80            | 0.630 | 1025              |
| B60         | 585               | 6.09            | 0.607 | 1428              |
| M100 + 6\% H\(_2\)O | 3.1            | 28.7           | 0.821 | 407               |
| M80 + 6\% H\(_2\)O | 3.8            | 57.5           | 0.696 | 92                |
| M60 + 6\% H\(_2\)O | 5.2             | 70.3           | 0.747 | 8.8               |
| E80 + 6\% H\(_2\)O | 86.8           | 0.600          | 6.9   | 6.1               |
| E60 + 6\% H\(_2\)O | 35.9           | 0.689          | 32    | 8.4               |
| iP100 + 6\% H\(_2\)O | 87.0          | 0.577          | 8.3   | 16                |
| iP80 + 6\% H\(_2\)O | 90.3           | 0.666          | 6.4   | 19                |
| iP60 + 6\% H\(_2\)O | 57.4           | 0.970          | 13.6  | 39                |
| B100 + 6\% H\(_2\)O | 113           | 0.619          | 7.9   | 15                |
| B80 + 6\% H\(_2\)O | 129           | 0.589          | 8.8   | 17                |
| iP80 + 6\% H\(_2\)O | 147           | 0.663          | 8.1   | 5.6               |
| iP60 + 6\% H\(_2\)O | 101           | 0.891          | 5.0   | 6.5               |
| aB100 + 6\% H\(_2\)O | 137           | 0.656          | 4.5   | 15                |
| aB80 + 6\% H\(_2\)O | 123           | 0.722          | 3.8   | 18                |

The low resistance of the mild steel in such an environment. This is documented by low polarization resistances \(R_{\text{p}}\) and increasing capacitances of an electric double layer \(C_{\text{dl}}\) (that are easier to form at the metal-environment interfaces in a more conductive and polar environment with higher ionic strength; see Table 2). Capacitance \(C_{\text{dl}}\) corresponds to an imperfect capacitor. This imperfection is characterized by the \(n\)-parameter that describes the distribution of the electric double layer on the electrode surface and depends, for example, on the surface homogeneity.

2.3. Cyclic Potentiodynamic Polarization. All calculated and evaluated data from the CPP after the iR drop compensation are summarized in Table 3. The first part of this table presents the results from the CPP curve parts that were measured by the shift from the cathode to anode potentials. The second part of the table presents the data that were evaluated from the reverse polarization parts of the CPP curves to which an opposite potential shift corresponds than the one in the previous case, that is, from the anode to cathode values. These results are subsequently discussed in the following subsections of this section.

It has to be mentioned that during the measurement of the cathode–anode CPP parts during the shift of the potentials to the anode area, substantial surface changes to the mild steel were observed that can influence and, thus, distort the evaluated data from the reverse polarization. The \(R_{\text{p}}, \beta_a, R_{\text{pp}},\) and \(i_p\) data presented in the second part of the table have, thus, a rather illustrative character and cannot be understood as absolute.

2.3.1. Influence of the iR Drop on the CPP and Its Compensation. The iR drop is a potential loss that is caused...
Environmental resistance in automatic compensation. The potential loss can significantly affect the CPP curves, it was necessary to additionally perform the measurement as the resistance of the environmental drop compensation (iR drop subtraction) was tested, but this method was found to be unfeasible for the high, and this led to the overcompensation of the part.

Environmental resistances are presented in Table 2.

| Environment       | $\beta_i$ (V/dec) | $\beta_o$ (V/dec) | $E_{corr}$ (mV) | $R_{cpp}$ (kΩ/cm²) | $i_{corr}$ (µA/cm²) | $T_{corr}$ (µm/year) |
|-------------------|-------------------|-------------------|-----------------|--------------------|--------------------|----------------------|
| M100 + 6% H₂O     | 0.10              | 0.27              | −30             | 533                | 5.8 × 10⁻²         | 6.0 × 10⁻²          |
| E100 + 6% H₂O     | 0.14              | 0.58              | −80             | 529                | 9.3 × 10⁻²         | 8.1 × 10⁻²          |
| E80 + 6% H₂O      | 0.20              | 0.22              | −151            | 435                | 1.0 × 10⁻²         | 1.1 × 10⁻¹          |
| E60 + 6% H₂O      | 0.51              | 0.77              | −168            | 1235               | 1.1 × 10⁻¹         | 1.0 × 10⁻¹          |
| iP100 + 6% H₂O    | 0.14              | 0.05              | −109            | 868                | 1.8 × 10⁻²         | 1.9 × 10⁻²          |
| iP90 + 6% H₂O     | 0.33              | 0.59              | 6               | 1475               | 6.0 × 10⁻²         | 6.0 × 10⁻²          |
| iP50 + 6% H₂O     | 0.22              | 0.18              | −131            | 1738               | 2.2 × 10⁻²         | 3.9 × 10⁻²          |
| B100 + 6% H₂O     | 0.23              | 0.62              | −223            | 1344               | 5.4 × 10⁻¹         | 1.2 × 10⁻²          |
| B80 + 6% H₂O      | 0.12              | 0.08              | −189            | 1022               | 2.1 × 10⁻²         | 6.0 × 10⁻²          |
| B60 + 6% H₂O      | 0.22              | 0.38              | −257            | 1456               | 4.1 × 10⁻²         | 4.2 × 10⁻²          |
| M100 + 6% H₂O     | 0.10              | 0.21              | −110            | 430                | 6.7 × 10⁻²         | 7.1 × 10⁻²          |
| E100 + 6% H₂O     | 0.03              | 0.26              | −150            | 85                 | 1.3 × 10⁻¹         | 1.2 × 10⁻¹          |
| E80 + 6% H₂O      | 0.12              | 0.11              | −321            | 26                 | 9.6 × 10⁻¹         | 2.8                |
| E60 + 6% H₂O      | 0.26              | 0.36              | −364            | 26                 | 9.4                | 73                 |
| iP100 + 6% H₂O    | 0.04              | 0.11              | −172            | 165                | 8.1 × 10⁻¹         | 4.1 × 10⁻¹          |
| iP80 + 6% H₂O     | 0.33              | 0.39              | −406            | 63                 | 1.2                | 9.3                |
| iP60 + 6% H₂O     | 0.32              | 0.23              | −403            | 49                 | 1.2                | 21.6               |
| iP40 + 6% H₂O     | 0.37              | 0.28              | −452            | 52                 | 1.2                | 5.0                |
| B100 + 6% H₂O     | 0.22              | 0.28              | −411            | 42                 | 1.2                | 6.7                |
| B80 + 6% H₂O      | 0.34              | 0.30              | −432            | 48                 | 1.5                | 7.9                |
| aE80 + 6% H₂O     | 0.24              | 0.23              | −225            | 11                 | 4.6                | 6.3                |
| aE60 + 6% H₂O     | 0.25              | 0.23              | −260            | 9                  | 5.8                | 11.2               |
| aB100 + 6% H₂O    | 0.24              | 0.24              | −241            | 25                 | 2.2                | 12.5               |
| aB80 + 6% H₂O     | 0.27              | 0.27              | −296            | 26                 | 2.2                | 15.1               |

The corrosion current density and corrosion rate calculated using the polarization resistance $R_{EIS,p}$ is measured using EIS before the CPP measurement; see Table 2. The corrosion current density calculated using the polarization resistance $R_{CPP,p}$ is evaluated from the relevant CPP part.

By the environmental resistance and cell geometry (it reflects the distance between the working and the reference electrode). Initially, the possibility of an automatic iR drop compensation was tested, but this method was found to be unfeasible for the measurement as the resistance of the environmental $R_e$ was too high, and this led to the overcompensation of the iR drop. For the CPP curves, it was necessary to additionally perform the iR drop compensation after measuring the curves without the automatic compensation. The potential loss can significantly influence the curve course and result in a curve deformation as demonstrated on Figure 3. For the iR drop subtraction, the environmental resistance $R_e$, obtained by the evaluation of the EIS spectra measured before the CPP measurement for each steel-environmental system, was applied. The values of this $R_e$ resistance are presented in Table 2.

From the agreement of the polarization resistances of the mild steel $R_{EIS,p}$ (evaluated from the EIS spectra) and (evaluated from the CPP after the iR drop compensation) presented in Tables 3 and 4, it can be concluded that the iR drop can be very well compensated additionally (ex post) in many cases with a minimum error. In particular, this is above expectations especially in the less conductive environments such as the uncontaminated alcohols and uncontaminated AGBs, where the iR drop values are the highest. In this case, high polarization resistances, which are stable at the time during the experiment, probably contribute to the good agreement of the results. The mild steel corrosion occurs at a minimum rate that has no significant effect on the system change during the experiment. The differences in the $R_{EIS,p}$ and $R_{CPP,p}$ resistances by 1 order of magnitude occur especially in conductive environments (the contaminated alcohols and AGBs), where the resistance of the mild steel is low and the corrosion rate is high. Because of the relatively low environmental resistance $R_e$ of the contaminated alcohols and their gasoline blends, the deformation of the CPP curves due to the iR drop is lower and more exhibited for the reverse polarization curve; see Figure 3. The difference between the $R_{EIS,p}$ and $R_{CPP,p}$ resistances at the level of 1 order of magnitude can be especially caused by the time development of the polarization resistance of the mild steel during the short term of the whole experiment. This change in the polarization resistance over a short time period can be then reflected in the CPP. In the following text, the CPP curves with the iR drop compensation are presented.

2.3.2. Influence of Alcohol Chain Length on Its Aggressiveness and Resistance of Mild Steel. Mild steel in the presence of pure and anhydrous alcohols has very good corrosion resistance and, thus, a low corrosion rate that is very similar for the many alcohols tested; see Table 4. The low aggressiveness of the pure and anhydrous alcohols is also evidenced by a slight shift in the cathode–anode CPP part toward lower corrosion current densities in dependence on the growing alcohol chain; see Figure 4. According to the CPP records presented in Figure 4, it is obvious that the corrosion potential of the mild steel $E_{corr}$ shifts toward negative values of the potential with the growing alcohol chain; also, see Table 3. The $E_{corr}$ values are consistent with the theory and with the increasing $pK_a$ values of the alcohols with the decreasing.
carbon number in the molecule; see Table 1. Methanol (the highest value of \( E_{\text{corr}} = -30 \text{ mV} \)), which has a lower \( pK_a \) than butanol (the highest value of \( E_{\text{corr}} = -223 \text{ mV} \)), more easily cleaves the proton and its higher activity results in shifting the CPP curve toward the more positive values of the potential. The CPP shift toward the more negative values can be influenced by the amount of dissolved oxygen that is easily involved in the depolarization reactions, and its solubility increases with the increasing length of the alcohol chain; see Table 1.

With the increasing length of the alcohol chain, we also observed the shift of the \( E_{\text{rp}} \) of the steel for the reverse polarization curves toward more positive values of the potential, where the steel is in a passive state; see Figure 4. The increasing resistance of the mild steel and the decreasing alcohol aggressiveness is documented by the increasing difference between the \( E_{\text{corr}} \) and \( E_{\text{rp}} \) potentials. The lowest difference of the potentials was measured in methanol, where the corrosion resistance of the steel is the lowest in contrast to the steel-butanol system; see Figure 4. During the passivation of steel in an environment of alcohols, the consumption of the dissolved oxygen occurs. On the surface of the steel, a layer of insoluble oxides (corrosion products) is formed, and this protects the steel against further corrosion. With the increasing amount of dissolved oxygen, which is the highest in butanol, the steel passivation appears to be easier and more intense. These conclusions are supported by the overall course of the CPP curves shown in ethanol, isopropyl alcohol, and butanol in Figure 4. In all these alcohols, no shift toward higher current densities occurs at the reverse polarization. The current densities at the reverse polarization are lower and no hystereses are formed unlike methanol. The highest activity of the \( H^+ \) protons and the lowest oxygen solubility in the methanol at the same time results in (i) a significant shift of the repassivation part of the CPP toward higher current densities (see the one order of magnitude higher values of \( i_{\text{rp}} \) than \( i_{\text{corr}} \) in Table 3) and (ii) the formation of a hysteresis loop at higher current densities. The size of the hysteresis loop is related to the surface changes during the anodic reaction, to the development of the extensive surface or pitting corrosion, and it also indicates a low passivation ability of the steel in the given environment.

2.3.3. AGBs and Their Aggressiveness on Mild Steel.

Gasoline added to the alcohols has, in many cases, a similar influence, and it has a positive effect on the repassivation kinetics of the steel; see Table 3. The measured corrosion rates of the mild steel are lower than in the environment of the pure alcohols. The addition of gasoline to the methanol and ethanol and the corrosion and repassivation potential of the mild steel \( E_{\text{corr}} \) and \( E_{\text{rp}} \) are influenced similarly; see Figure 4. With the increasing gasoline content in the AGBs, the corrosion potential is shifted toward more negative values. Conversely, the repassivation potential shows an upward trend up to the positive values. This effect is probably related to the increasing solubility of oxygen in the blend, which increases with the increasing gasoline content, in which oxygen is more soluble than in the pure alcohols; see Table 1. Oxygen participates in the depolarization cathode reactions, and their course is influenced by the amount of the dissolved oxygen in the

Table 4. TAN and pH Values at 25 °C of Some of the Selected Tested Environments

| environment | pH  | TAN (mg KOH/g) |
|-------------|-----|----------------|
| M100        | 6.80| <0.01          |
| E100        | 6.84| <0.01          |
| B100        | 6.86| <0.01          |
| E100 + 6% H\(_2\)O | 6.98 | <0.01       |
| B100 + 6% H\(_2\)O | 7.14 | <0.01       |
| aE80 + 6% H\(_2\)O | 5.65 | 0.081        |
| aE60 + 6% H\(_2\)O | 5.79 | 0.073        |
| aB100 + 6% H\(_2\)O | 5.69 | 0.092        |
| aB80 + 6% H\(_2\)O | 5.88 | 0.073        |

Figure 3. Influence of \( iR \) drop on the CPP curve of mild steel in the environment of (a) methanol with 6 vol % of water and 40 mg/kg of sodium chloride, (b) \( n \)-butanol—gasoline blend B80.

Figure 4. CPP curves of the mild steel measured in pure alcohols.

The increasing resistance of the mild steel and the decreasing alcohol aggressiveness is documented by the increasing difference between the \( E_{\text{corr}} \) and \( E_{\text{rp}} \) potentials. The lowest difference of the potentials was measured in methanol, where the corrosion resistance of the steel is the lowest in contrast to the steel-butanol system; see Figure 4. During the passivation of steel in an environment of alcohols, the consumption of the dissolved oxygen occurs. On the surface of the steel, a layer of insoluble oxides (corrosion products) is formed, and this protects the steel against further corrosion. With the increasing amount of dissolved oxygen, which is the highest in butanol, the steel passivation appears to be easier and more intense. These conclusions are supported by the overall course of the CPP curves shown in ethanol, isopropyl alcohol, and butanol in Figure 4. In all these alcohols, no shift toward higher current densities occurs at the reverse polarization. The current densities at the reverse polarization are lower and no hystereses are formed unlike methanol. The highest activity of the \( H^+ \) protons and the lowest oxygen solubility in the methanol at the same time results in (i) a significant shift of the repassivation part of the CPP toward higher current densities (see the one order of magnitude higher values of \( i_{\text{rp}} \) than \( i_{\text{corr}} \) in Table 3) and (ii) the formation of a hysteresis loop at higher current densities. The size of the hysteresis loop is related to the surface changes during the anodic reaction, to the development of the extensive surface or pitting corrosion, and it also indicates a low passivation ability of the steel in the given environment.

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environment. The oxygen depolarization can occur according to the reaction presented below

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \]

At a higher concentration of the dissolved oxygen in a blend, more \( \text{OH}^- \) ions are formed during the oxygen depolarization and this results in the shift of the \( E_{\text{corr}} \) toward more negative values. The influence of the dissolved oxygen on the course of depolarization reactions is also evidenced by the lower \( E_{\text{corr}} \) values of the mild steel (Figure 5b and Table 3) in the EGBs. In the EGBs, the amount of the dissolved oxygen is higher than in the methanol–gasoline blends (MGBs) as the oxygen solubility in the methanol is lower than in the ethanol, see sub-section 2.3.2 and Figure 4.

The higher differences between \( E_{\text{corr}} \) and \( E_{\text{rp}} \) in Figure 5b in comparison with Figure 5a indicate a better passivation ability of mild steel in an EGB; see also Table 3. The higher passivation ability of the steel in the EGBs and lower corrosion aggressiveness of the EGBs is also obvious from the overall CPP course, where the mild steel shows lower values of the anode current density at the reverse polarization (see Figure 5b) in comparison with the MGBs. Conversely, Figure 5 clearly illustrates the higher anode current density at the reverse polarization and hysteresis at higher current densities which decreases with the increasing amount of gasoline in the MGBs. These conclusions can be also supported by the values of \( i_{\text{p}} \) in Table 3, where 1 order of magnitude higher values was measured in the MGBs. The lower \( i_{\text{p}} \) values are associated with the higher passivation ability and the formation of a protective layer on the steel surface that is not soluble in the environment.

2.3.4. Influence of the Contamination of Alcohols and AGBs. According to polarization characteristics and corrosion rates presented in Table 3, the contamination of alcohols and AGBs had a substantial influence on their corrosion aggressiveness and resistance of the mild steel which is in accordance with the data published previously for EGBs.10

The electrochemical behavior of the mild steel in methanol and the influence of the contained water and chlorides is obvious from Figure 6a. The relevant graph confirms the results of the OCP measurements that were discussed in Section 2.1. The addition of a 6 vol % of water with 40 mg/L of sodium chloride influences the shift of the corrosion potential toward negative values and, at the same time, the shift of the entire curve to higher current densities which is evidence of an increasing corrosion rate; see Table 3. The hysteresis loop presented in Figure 6a and polarization data evaluated from the reverse polarization in Table 3 indicate the very poor passivation ability of mild steel and their susceptibility to extensive pitting corrosion in the environment of the contaminated methanol. For anhydrous methanol, a lower increase in the current density with the increasing potential is visible from the anode part, in comparison with the cathode part, for steel in the contaminated methanol. Mild steel could be closer to a passive state in anhydrous methanol (potential up to 150 mV), but, despite this, the high susceptibility to corrosion is indicated by the hysteresis and the data presented in Table 3. The highlighted part of the cathode curve indicates the achievement of diffusion control of the cathode reaction.

The mild steel in the ethanol environment shows, according to Figure 6b, a different behavior in comparison with the

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**Figure 5.** CPP curves of the mild steel measured in methanol (a) and ethanol (b) in the gasoline blends.

**Figure 6.** CPP curves of the mild steel measured in methanol (a) and ethanol (b) with no contamination and with contamination by a 6 vol % of water and 40 mg/L of sodium chloride.
methanol; see Figure 6a. The different behavior is associated with the higher aggressiveness of the methanol, which has a lower $pK_a$ (see Table 1), is easier to deprotonate and it protonates the water present in the methanol. The mild steel in the anhydrous ethanol (water content 900 mg/kg), unlike the anhydrous methanol (670 mg/kg), shows no hysteresis at higher current densities. The data in Table 3 indicate good passivation kinetics and mild steel resistance in ethanol. The contamination of the ethanol results in the formation of the hysteresis, which is not as significant as for methanol. The better repassivation ability of mild steel in the contaminated ethanol is also obvious from Table 3, where $E_{rp}$ is mostly shifted toward positive values and the entire reverse polarization shift slightly toward the lower current densities than for methanol; see also $i_{corr}$ in Table 3.

From the course of the mild steel CPP in Figure 7a, it is obvious that the contamination of all of the tested alcohols significantly reduces the difference between $E_{corr}$ and $E_{rp}$ compared with Figure 4. This influence of contamination indicates the substantial deterioration of the repassivation kinetics of the mild steel in the environment of the contaminated alcohols. From the position of the CPP curves in Figure 7a, the influence of the oxygen solubility in the contaminated fuels on the mild steel resistance can be deduced also. The level of oxygen solubility in the contaminated ethanol and isopropyl alcohol contributes to the passivation of the mild steel that results in the shift in the CPP toward lower current densities; also, see the values of $i_{corr}$ and $i_{np}$ in Table 3. This is probably the initial state of passivation that was demonstrated for the contaminated ethanol already in our previous study.10 This state is unlikely to be persistent and will likely be violated by the influence of the increasing concentration of the corrosion products in an environment, which can gradually catalyze the subsequent corrosion development. For the contaminated methanol, the amount of the dissolved oxygen is not high enough to allow the repassivation kinetics of the mild steel to form a sufficiently resistant passive film (high hysteresis and $i_{np}$ value), although the low $i_{corr}$ values point out to a low corrosion rate. Conversely, the oxygen solubility is the highest in the contaminated butanol. Considering the lowest values of $pK_a$ for butanol and its lowest aggressiveness from all of the tested pure alcohols, the oxygen content, at the same contamination level, plays a substantial role in increasing the butanol aggressiveness and mild steel corrosion. The hysteresis indication in the anode CPP part and the shift of the entire curve toward higher current densities suggests the susceptibility to a pitting corrosion due to the presence of chlorides and the reduction of the corrosion resistance of the mild steel in the contaminated butanol.

The influence of oxygen solubility on the mild steel corrosion can also be observed in the contaminated AGBs; see Figure 7b,c. With the increasing gasoline content in the contaminated EGBs, the oxygen solubility increases and this also leads to an increase in the blend aggressiveness. Such an increased aggressiveness is manifested by the shift of the curves toward higher current densities, as evidenced in Figure 7b, and by the increasing $i_{corr}$ values; see Table 3. The oxygen solubility, dependent on the gasoline content of the contaminated blend, also has an effect on the repassivation kinetics of the mild steel. The gasoline content of 20 vol % significantly deteriorates the repassivation kinetics and the highest shift of the repassivation CPP part for the E80 blend indicates the worst corrosion resistance of the mild steel. This low resistance is also evidenced by the increasing hysteresis in the anode CPP part. For the contaminated isopropyl AGBs, such hysteresis was not observed (see Figure 7c), but despite this, the increasing oxygen content in the blend and the presence of water with sodium chloride significantly deteriorates the corrosion resistance of the mild steel as evidenced by the $v_{corr}$ corrosion rate values in Table 3. With the increasing content of gasoline to up to 60 vol % in the isopropyl AGBs, the corrosion rate of the steel significantly increases. The increase in the corrosion rate is also evident from the CPP shift toward higher current densities for iP80 and iP60. In addition, the very poor corrosion resistance of the mild steel in the contaminated iP80 and iP60 blends is indicated by the overlap of the CPP parts (reverse polarization with the cathode–anode) in Figure 7 and the significantly decreasing difference between the $E_{corr}$ and $E_{rp}$ values, which is minimal here.
The influence of organic acids, which may come from the alcohol production processes or be formed as oxidation products during the long-term storage of the AGBs, was simulated by the addition of 80 mg/L of acetic acid. The relevant CPP records are presented in Figure 8. The addition of acetic acid increases the activity of the H⁺ protons (see the pH and TAN values in Table 4) which, in all of the tested cases, was manifested by the shift of the $E_{\text{corr}}$ values to the positive potential values, which is, in accordance with theory and previous results, measured in the environments of pure alcohols in dependence on $pK_a$. In all of the tested steel-environment systems, the anode current density at the reverse polarization increases, hysteresis also increases, and the $E_{\text{rp}}$ values shift toward more negative values than the $E_{\text{corr}}$ values. This indicates the decreasing corrosion resistance of the mild steel and practically no passivation abilities with the increasing content of acetic acid. The results presented in Table 3 point to a two-fold increase in the corrosion rate of the mild steel in comparison with the contaminated alcohols and their blends with gasoline without acetic acid.

Gasoline content and the amount of dissolved oxygen in the contaminated AGBs containing acetic acid significantly affect the course of depolarization reactions, and an increase in the corrosion rate of the mild steel occurs. This corrosion rate is increasing with the gasoline content in the blend as indicated by the calculated corrosion rates presented in Table 3. According to Figure 9, the shift of the $E_{\text{rp}}$ values toward more negative values becomes more significant and, thus, the corrosion resistance of the mild steel decreases as well.

Finally, it should be noted that the content of the water, chlorides, and organic acids has a crucial effect on the corrosion of mild steel and the corrosion aggressiveness of the alcohols and their blends with gasoline. This aggressiveness and resistance are significantly influenced by the physical and chemical properties of the alcohol and its chain length. Among these physical and chemical properties, especially, the oxygen solubility and $pK_a$ of an alcohol are the most important. For AGBs, the content of the gasoline in the blend, which affects the oxygen solubility and the overall aggressiveness of the blend, is the most significant. It is likely that although gasoline does not promote aggressive corrosion of mild steel, in many cases, the aggressiveness of the AGBs increases up to the gasoline content of 40 vol %. This increasing aggressiveness can be given by the synergistic effect of the dissolved oxygen and water. Moreover, it is likely that a further increase in the gasoline content in the AGBs to values higher than 40 vol % would result in a decrease in the aggressiveness as the synergic effect would be impaired due to the decreasing water solubility in the blends; see the results measured in the environment of the contaminated isopropyl alcohols–gasoline blends.

3. CONCLUSIONS

Using CPP, we have proven the substantial influence of the alcohol chain length and its physical and chemical properties (especially $pK_a$ and oxygen and water solubility) on the corrosion aggressiveness of alcohols and AGBs to mild steel. The oxygen solubility and the course of the depolarization reactions are also influenced by the gasoline content. In general, the corrosion resistance and repassivation ability of the mild steel increase with the increasing alcohol chain length as a result of the increasing oxygen solubility and increasing $pK_a$. The effects of the environments of the pure alcohols for the mild steel are rather of a passivation character. The very good resistance and passivation ability of mild steel was especially...
shown in the pure butanol. When alcohols and their gasoline blends are contaminated by water, chlorides, and organic acids, the higher oxygen content, conversely, decreases the corrosion resistance of the mild steel, and a large increase is observed in the corrosion rates, even up to 4 orders of magnitude.

The CPP was found to be a suitable method even for the measurements in nonaqueous environments of alcohols and their gasoline blends. In these environments, the CPP gives results having a very good predictive ability for the corrosion rates of metals, and their ability to be passivated, or resistant to corrosion, in a given environment.

4. EXPERIMENTAL SECTION

For the measurement and the preparation of the AGBs, methanol, ethanol, isopropyl alcohol, and n-butanol were used (all p.a., Penta a.s., the Czech Republic, with the alcohol content ≥99.9% and water content ≤900 mg/kg). The blends of these alcohols with gasoline were prepared (AGBs) so that the alcohol content was 40, 60, and 80 vol %.

The weight losses m in (g/m²·h) of the tested materials for the chosen test period (3600 s) were obtained; see eq 3.

$$m = A \cdot i_{\text{corr}} \cdot t$$  

where $$A = \frac{M}{z \cdot F}$$

$$A$$ is the proportionality constant in kg/C, which is designated as the electrochemical equivalent of the substance; $$M$$ is the molar mass of steel (55.8 g/mol); $$z$$ is the number of exchanged electrons; and $$F$$ is the Faraday constant (9.6485 × 10⁸ C/mol).

The weight loss was then converted using the steel density ρ (7860 kg/m³) to the corrosion rate $$v_{\text{corr}}$$ or $$v_p$$ in mm/year according to eq 4.

$$v_{\text{corr}} = 8.76 \cdot \frac{v_p}{\rho}$$

mg/L of sodium chloride (p.a., 99.9%, Penta a.s., the Czech Republic), and 80 mg/L of acetic acid (p.a., 99.9%, Penta a.s., the Czech Republic).

The sample labeling for the uncontaminated fuels consisted of a letter or letters (M—methanol, E—ethanol, iP—isopropyl alcohol, B—n-butanol) and a number describing the alcohol content in the AGBs. For the contaminated fuels, the labeling consists of the labeling for the relevant uncontaminated fuel amended by the description of the contamination. For the fuels contaminated by water and sodium chloride, this description is as follows: 6 vol % H₂O. For the fuels contaminated by water, sodium chloride and acetic acid, an “a” has been added before the letter(s) characterizing the alcohol, for instance: aB80 + 6% H₂O.

The electrochemical measurements were performed on a Gamry Reference 600 potentiostat controlled by the Gamry Framework 5.21. software at an ambient temperature in a three-electrode arrangement in a cell containing 100 mL of a tested fuel. The cell was placed in a Faraday cage. The electrode system consisted of (i) a working electrode from mild steel, cylindrical in shape with a surface area of 2.4 cm², (ii) an auxiliary platinum electrode, and (iii) a reference silver chloride electrode for the nonaqueous environments with a bridge containing a 0.1 mol/L solution of lithium chloride in ethanol. The working electrode was treated by grinding and wet polishing on a 1200 grit abrasive paper before the measurement, then degreased with acetone (p.a.), and dried with paper. The cell geometry and the electrode system arrangements were already presented elsewhere.

At the beginning of each measurement, the corrosion potential was measured during its stabilization (OCP) for 1 h. Then, the electrochemical impedance spectra at an amplitude of 10 mV in a frequency range of 1 MHz to 10 mHz were measured. At the end, the CPP was measured with a scanning rate of 2 mV/s in the range of 1000 mV against the corrosion potential from the negative to the positive potentials and back again.

The Tafel coefficient for cathode β_c and anode area β_a/polarization resistance R_p ($$R_p$$), and corrosion potential E_{corr} ($$E_p$$) were obtained by the evaluation of the polarization curve. The corrosion current density $$i_{\text{corr}}$$ was obtained from the Stern—Geary equation, eq 2.

$$i_{\text{corr}} = \frac{\beta_c \cdot \beta_a}{2.3 \cdot (\beta_a + \beta_c)}$$

The values of the corrosion current density and the weight losses m (g/m²·h) of the tested materials for the chosen test period (3600 s) were obtained; see eq 3.
The total acid number (TAN) and pH values were measured to characterize the aggressiveness of the tested fuels. The TAN measurements were performed in accordance with the IP 177/96 and ASTM D664-89 standards on an automatic titrator DMS TITRINO 716 with a potentiometric detection of an equivalent point. The pH measurements were performed on an inoLab pH/Cond Level 1 instrument at an ambient temperature. The obtained TAN and pH results are presented in Table 4.

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■ ACKNOWLEDGMENTS

This research was funded from the institutional support for the long-term conceptual development of the research organization (company registration number CZ60461373) provided by the Ministry of Education, Youth and Sports, the Czech Republic.

■ ABBREVIATIONS

AGBs alcohol–gasoline blends
CPE constant phase element
CPP cyclic potentiodynamic polarization
EGBs ethanol–gasoline blends
EIS electron impedance spectroscopy
EU European Union
iP isopropyl alcohol
MGBs methanol–gasoline blends
OCP open-circuit potential
TAN total acid number

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