

Influence of gasoline hydrocarbons on electrochemical processes during steel corrosion in ethanol

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Although corrosion mechanisms in ethanol have been discussed extensively, conclusions cannot always be extended to bioethanol and gasoline mixtures. In the presence of water, phase separation can take place leading to rapid corrosion on the bottom of reservoirs, tanks, lines, etc. In this study electrochemical experiments were developed to investigate the corrosion mechanisms on horizontally immersed low carbon steel electrodes. The electrolytes represented simulated biofuels with 100, 85, 70% and 33% vol. of dehydrated ethanol plus 1:1 mixture of n-heptane and toluene with or without addition of water, acetic acid and chlorides. Electrodes were laid into flasks with simulated biofuels and periodically removed to measure Electrochemical Impedance Spectroscopy (EIS) parameters. Counterintuitively, the corrosion accelerated with higher amounts of hydrocarbons most likely due to two main factors. Although electrochemical behaviour of blends with 15% hydrocarbons or less was similar to that of pure ethanol, hydrocarbon increase to 30% produced a big change in kinetics. Another factor could be minor amounts of water, which might lead to phase separation and preferential adsorption of water aggregates on horizontal metal surfaces. The phase separation could intensify in the presence of chlorides. If amounts of hydrocarbon and ethanol are similar in biofuel, great care must be taken to prevent the access of chlorides and other corrosion precursors.

Key words: corrosion, ethanol, electrochemistry, fuel

INTRODUCTION

Widespread acceptability of gasolines with 4–5% bioethanol as well as success of E-85 biofuel, which contains 85% bioethanol, ignites some interest in producing gasoline with intermediate amounts of bioethanol like 20, 30% or similar. Also, such ratios between bioethanol and hydrocarbons quite frequently occur in gas tanks of flex-fuel cars, which irregularly fill up with E-85 and conventional gasoline. Random fuelling with different brands of gasoline leads to the varying bioethanol : hydrocarbon ratio anywhere from 0.05 to 0.85. Often resistance to rust formation of such fuel mixtures is viewed as better than that of E-85 because less ethanol is assumed to improve corrosion resistance. Corrosion mechanisms have already been investigated in detail with ethanol concentrations below 20% [1–3]. However, with increasing oxygenate contents the mixing between ethanol and gasoline becomes highly non-ideal [4] leading to major phase separation effects. Hygroscopic ethanol acceler-

ates water absorption, which facilitates dividing the single-phase ethanol–gasoline mixture into two phases: 1) asoline on top and 2) water–ethanol on the bottom. As a result, the separated water–ethanol phase causes the metal to corrode. Extensive phase separation studies in ethanol and hydrocarbon mixtures [5] have shown that less than 3% water is sufficient to cause phase separation in 50% ethanol mixture with hydrocarbons, especially at 0 °C or below. Due to these complexities, corrosion research is scarce on fuels, where amounts of gasoline and bioethanol are similar.

Nevertheless, with the increasing usage of bioethanol as a gasoline component it is inevitable that gasoline : ethanol blends, which have comparable volumes of each component, become commonplace. Therefore, it is necessary to better understand the main corrosion mechanisms under circumstances, when neither ethanol nor gasoline could be viewed as overwhelmingly dominant. Since conventional gasolines contain a great variety of hydrocarbon molecules, it would be difficult to establish specific chemical reactions or transformations, responsible for corrosion-related processes. Such structural diversity presents a problem

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for many other fuel research fields and, consequently, it has become customary that isooctane, i.e. 2,4,4-trimethyl pentane, n-heptane and toluene are the most representative components of gasoline for various investigations [6]. For example, toluene-reference fuels, made from just those three compounds, were subjected to extensive studies of ignition and flame propagation [7–8]. Isooctane and n-heptane might have significant differences under combustion conditions, however, at ambient environment their chemical and physical properties are not so distant. Both of them are highly non-polar fully saturated alkanes of similar molecular weight (114.2 and 100.2 g/mol, respectively). Therefore, it would be justifiable to remove isooctane in order to further simplify the system and to delegate a 1:1 mixture of n-heptane (C_7H_{16}) and toluene (C_7H_8), both being hydrocarbons with seven C atoms, for representing the gasoline portion of simulated fuel.

Since phase separation in ethanol containing fuels might play a significant role, rust formation could proceed differently on horizontal and vertical surfaces [9]. The difference in densities of water and fuel is more than sufficient to force the water phase to the bottom. As a result, such phase separation is much less likely to impact vertical surfaces, compared to horizontal surfaces. Communication with the personnel, who deal with biofuel wholesale in Lithuania, revealed that ethanol reservoirs corrode mostly on the bottom and further substantiated the above supposition. Therefore, horizontal placement of electrodes was selected for this study.

EXPERIMENTAL

Most materials and equipment were equivalent to those reported previously [10]. Briefly, dehydrated ethanol contained less than 0.1% water, while n-heptane, toluene, acetic acid and ammonium chloride were more than 99% pure. Low carbon steel contained (% wt.): Fe > 99.2, C ~ 0.13, Mn ~ 0.25–0.6, P ~ 0.04 and S ~ 0.05. The electrolytes were prepared by pouring the necessary volumes of ethanol and the hydrocarbon (C7) blend into an Erlenmeyer flask and shaking. When required, the amounts of corrosion precursors (water, acetic a. and chlorides) were calculated as weight percentages of the ethanol portion, since EN15376 “European Fuel Ethanol Specification” requires that their concentrations should not exceed the following limits: 3 000 ppm water, 70 ppm CH_3COOH and 20 ppm Cl^- . The latter two were incorporated by initially pre-dissolving 0.7 g acetic acid and 0.3 g anhydrous NH_4Cl in 99 g deionized water, which was produced in a reverse osmosis system Demiwa™ 10 Rosa (Watek, Czech), resulting in conductivity below 1 $\mu S/cm$. The obtained solution was added into ethanol at 1% wt., leading to 70 ppm CH_3COOH and 20 ppm Cl^- in the ethanol portion. This was followed by blending in the remaining % wt. of deionized water to reach the needed concentration before C7 addition.

Table. Electrolyte compositions of C7 hydrocarbons (i. e. 1:1 mix of n-heptane and toluene by weight) and ethanol (sample code begins with “E”), which was either dehydrated or contained 5% deionized water (“W”) or corrosion precursors (“P”), i. e. 5% water with 70 ppm CH_3COO^- and 20 ppm Cl^-

Sample code	% wt. ethanol	% wt. C7	% wt. water	ppm precursors
E33	33.6%	66.4%	–	–
E70	70.5%	29.5%	–	–
E85	85.3%	14.7%	–	–
E100	100%	–	–	–
PE33	33.4%	65.1%	1.7%	33 ppm
PE85	81.7%	14.1%	4.2%	85 ppm
WE33	33.4%	65.1%	1.7%	–
WE85	81.7%	14.1%	4.2%	–
WE100	95%	–	5%	–

The electrolytes were coded based on ethanol contents (“E”), absence or presence of 5% wt. water (“W”) in the ethanol portion as well as the corrosion precursors (“P”) at 70 ppm CH_3COOH and 20 ppm Cl^- . The number after the “E” indicated the volumetric percentage of ethanol. The compositions of the blends are listed in the Table. For example, the code “PE70” indicates a sample, which has 30% vol. C7 (i. e. 1:1 n-heptane : toluene by weight) and 70% vol. pre-blended mixture of ethanol with 5% wt. water, 70 ppm CH_3COOH and 20 ppm Cl^- (both by weight).

Corrosion experiments were performed on the steel discs of 15 mm diameter, whose one side was polished in a Tegramin-25 machine (Struers Inc., USA) using #320 abrasive cloth of SiC, followed by water-ethanol based diamond pastes of 9 μm , 3 μm and 1 μm sizes. The mirror-like polished discs were washed with deionized water, dried with a lint-free napkin and placed into a capped jar, filled with argon gas. Every time after opening the jar, it was purged with Ar before closing.

Each corrosion test involved a number of cycles, consisting of two distinct stages: 1) long term immersion and 2) electrochemical measuring (Fig. 1). The first stage of every cycle in the corrosion experiment involved laying the discs horizontally on the bottom of frit-capped 150 mL Erlenmeyer flasks with 50–80 mL of a biofuel sample. Without touching each other, one or several discs were placed into every flask with a polished side facing upwards. After a specified duration of long-term immersion the electrode was removed and gently wiped with filter paper. Within 4 to 5 minutes after removal, the cleaned electrode was mounted into an empty 3-electrode electrolytic cell, which was specially adapted for the low conductivity media as described below. The cell was immediately filled with the same blend from the flask using a glass pipette, equilibrated for 9 to 11 minutes, and electrochemical characteristics were measured.

The electrochemical measurements in the specially adapted cell were performed using a Potentiostat/Galvanostat/Frequency Analyzer Autolab 302 (Eco Chemie, B. V.,

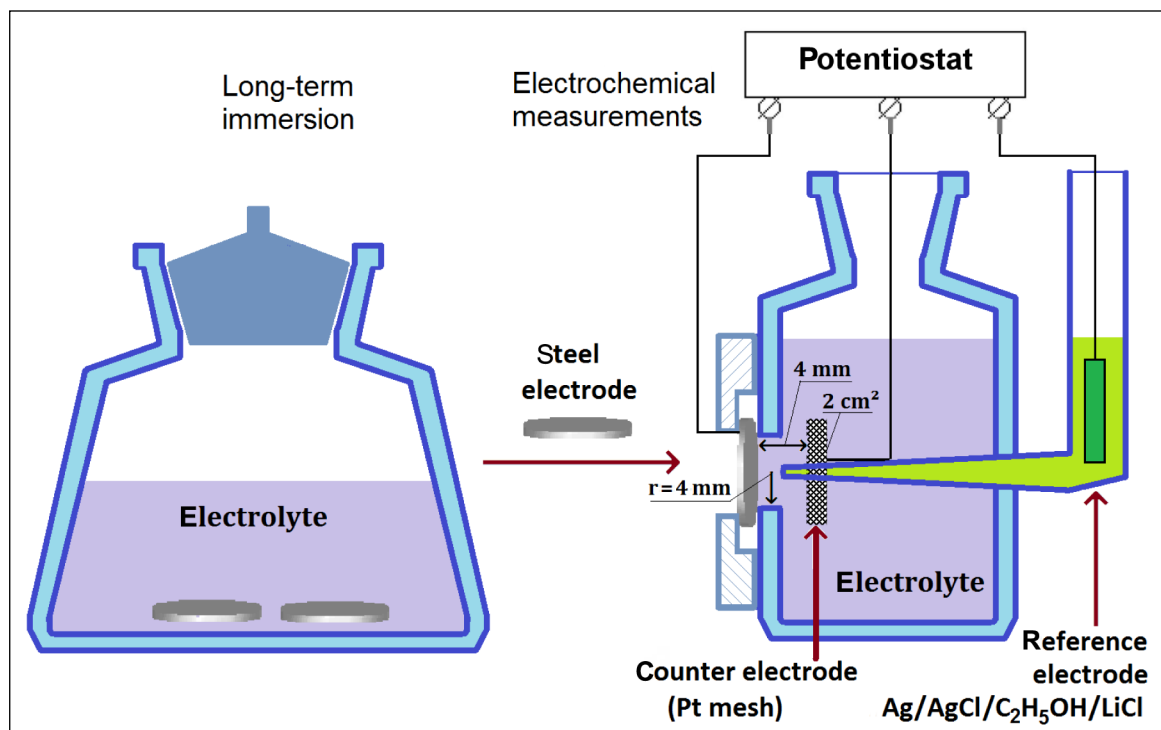


Fig. 1. Two stages of one corrosion test cycle: 1) immersion of horizontal discs in a glass reservoir; 2) determination of electrochemical parameters on vertically placed discs in a specially adapted 3-electrode cell

the Netherlands). The area of the electrode surface exposed to the electrolyte was 0.5 cm^2 . A Pt mesh of 2 cm^2 area was used as a counter electrode, see Fig. 1. A LiCl-fortified silver-silver chloride reference electrode for ethanol ($\text{Ag}/\text{AgCl}/1 \text{ M LiCl}$ in EtOH) was used in this study as described [11]. The distance between the counter electrode and the working electrode was fixed at 4 mm and the distance between the capillary tip of the reference electrode and the working electrode was fixed at 2 mm for every test. The impedance was measured with an applied AC voltage of 10 mV in the frequency range from 1 000 Hz to 0.005 Hz. Solutions were used under ambient conditions without aeration, i. e. “static air”.

RESULTS AND DISCUSSION

The study focused on three distinct topics: 1) effects of hydrocarbon contents and additions of water and corrosion precursors, 2) influence of immersion duration on polarization resistance, and 3) visual examination of corrosion and phase separation. Consequently, the results are discussed in this order.

Effects of water, corrosion precursors and hydrocarbon contents

The cell design assured that electrochemical measurements can be performed in relatively low conductivity media, such as E33, i. e. 33% vol. of dehydrated ethanol in C7, represented by 1:1 mix by weight of n-heptane and toluene. For the employed electrolytic cell this was not the lowest limit

of conductivity. Further tests, which have not been reported here, showed that it was possible to study even less conductive blends. The measurements were performed using Electrochemical Impedance Spectroscopy (EIS), interpreting the measured EIS spectra both as Bode plots (Fig. 2) and as capacitive semicircles on Nyquist plots (Fig. 3).

Large influence of C7 contents on the impedance and phase angle is evident in the dehydrated electrolytes. While higher conductivity blends E100 and E85 show quite similar electrochemical characteristics, the lower conductivity blends E70 and E33 behave very differently. The differences between E85 and E70 are particularly puzzling. Increase in C7 contents from 15 to 30%, respectively, would not be expected to cause dramatic transformations in kinetic mechanisms because toluene and n-heptane are relatively inert and non-polar. In addition, their amount is smaller than the amount of ethanol, and Bode plots show little variation with C7 addition from 0% in E100 to 15% in E85. Therefore, significant changes in kinetics with just somewhat higher hydrocarbon contents would be quite counter-intuitive.

However, with the increase of C7 from 15 to 30% vol. in E70 the electrochemical mechanisms on steel surface undergo a notable transformation. Phase angle variation becomes significantly different and attains an intermediate character between E85 and E33. Increase in impedance values at low frequencies suggests that the polarization resistance, R_p , might be much higher in E70. Such transformation might not be explained solely through chemical processes. However, when the amount of non-polar hydrocarbons goes up from

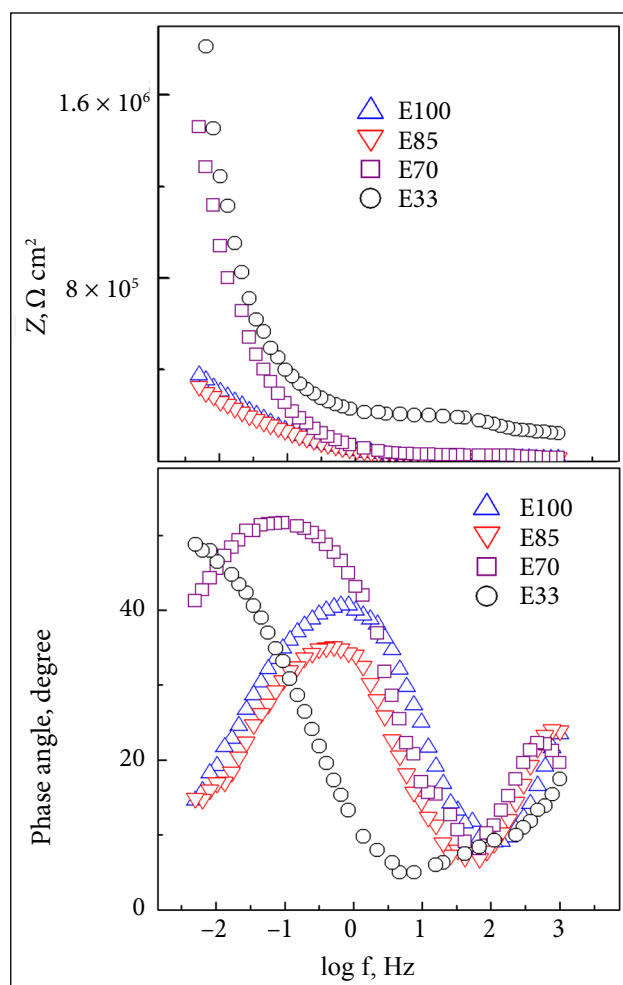


Fig. 2. Bode plots of electrochemical impedance and phase angle of C7 blends with 33, 70, 85% and 100% ethanol after 5 h immersion

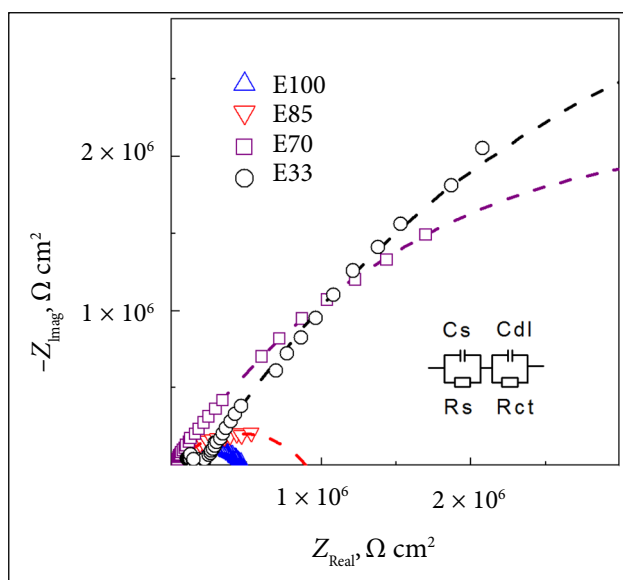


Fig. 3. Nyquist plots of electrochemical impedance and phase angle of C7 blends with 33, 70, 85% and 100% ethanol after 5 h immersion. Equivalent Electrical Circuit (EEC) for data fitting is shown on the right

15 to 30% vol., solvation mechanisms might be affected quite significantly. In terms of molar concentrations, this increase translates to change of ethanol concentration 92.4% mol. \rightarrow 83.4% mol., n-heptane 3.6% mol. \rightarrow 8% mol. and toluene 4% mol. \rightarrow 8.6% mol. Obviously, much fewer ethanol molecules become available to surround each hydrocarbon molecule, from 12 to 5 approx. Such transformation is likely to affect the double layer formation, molecular packing and related phenomena substantially. However, the experimental methodology did not provide the means to investigate these suppositions in more detail.

Since the impedance values do not approach a plateau in Bode plots (Fig. 2), it is quite problematic to obtain sufficiently reliable values of polarization resistance, R_p . Therefore, the EIS data was also transferred into Nyquist plots (Fig. 3) for the R_p calculation. The observed trends suggest that in the case of electrolytes with low conductivities, E33 and E70 in particular, the EIS data cannot be collected to complete a full semicircle on Nyquist plots, as compared to E100. Nevertheless, it appears that with higher conductivity the shape of semicircles becomes better expressed and might enable the extrapolation of impedance values, which could not be measured. The data fitting approach on Nyquist plots has often been used in previous EIS studies of ethanol electrolytes [12–13], therefore, it is reasonable to expect that the impedance values from low conductivity electrolytes could be extrapolated in the same manner. However, despite the fact that EIS at very low conductivities could still be recorded, data fitting of poorly conductive samples introduced major uncertainties and therefore the experiments were limited to blends with at least 33% vol. ethanol.

The data fitting approach for EIS of ethanol and C7 blends with or without water and corrosion precursors was based on the Equivalent Electrical Circuit (EEC) concept. An EEC of two sequential RC circuits was proposed to represent the impedance characteristics in the blends (Fig. 3). It has been customary to relate the first RC circuit of the EEC to the solution resistance R_s and its capacitance C_s . In ethanol-based electrolyte, these parameters can be represented by the resistance of ethanol blends and their capacitance between the working steel electrode and the reference electrodes.

Another RC circuit is composed of R_{ct} and C_{dl} , which are accepted to represent the resistance of charge transfer between the steel surface and electrolyte and the capacitance of a double layer on the working steel electrode. Using such EEC, the resistance and capacitance values were selected to produce the best approximation of the measured electrochemical impedance trends (Fig. 3).

Application of such methodology was extended to the blends with water and corrosion precursors. Their inclusion resulted in significant changes of the electrochemical patterns, as demonstrated by Bode plots (Fig. 4). Nevertheless, the behavior of sample pairs with 0 and 15% C7 remained quite similar. Their impedance was similarly affected by frequency and phase angle variations showed the same patterns.

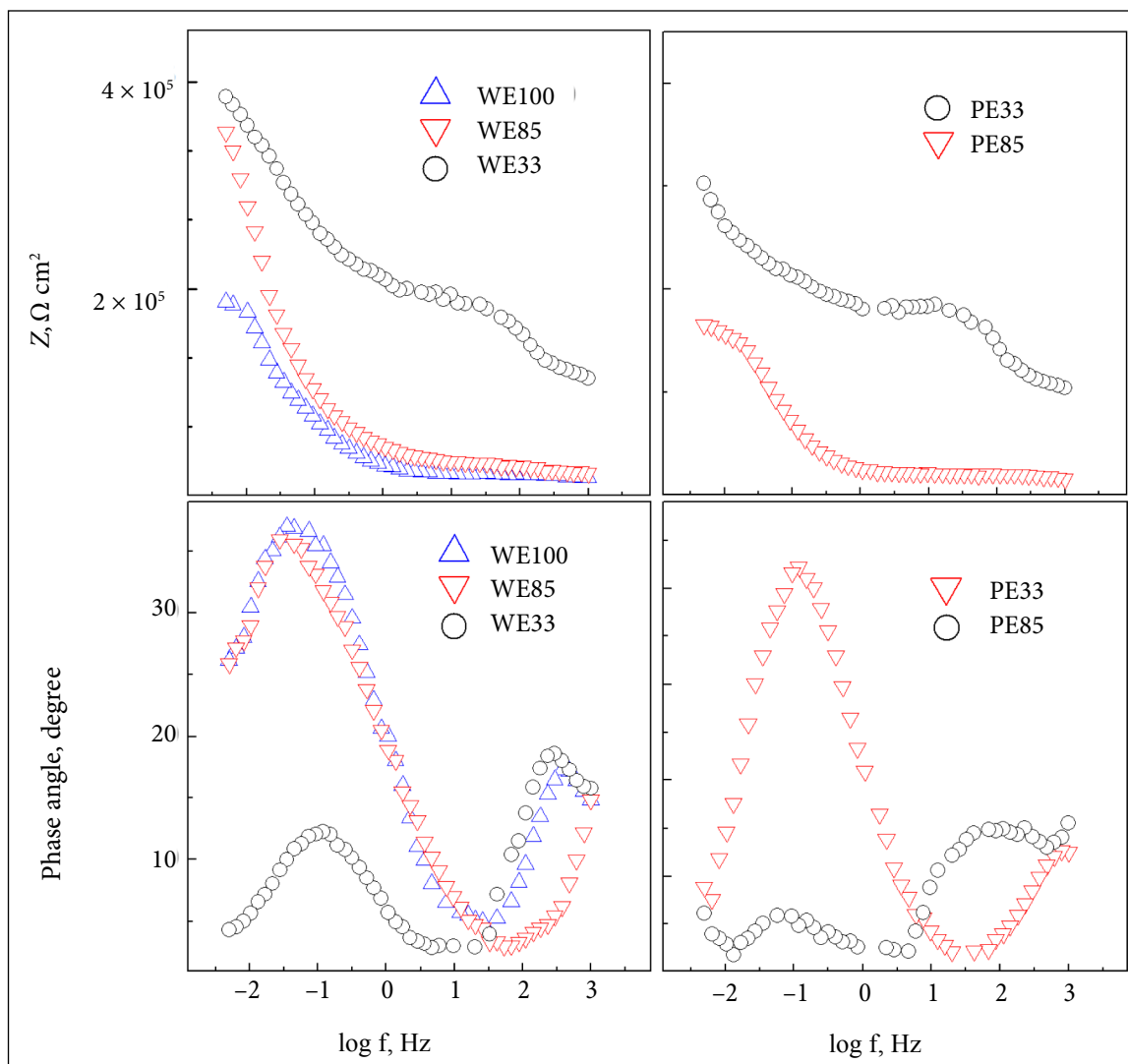


Fig. 4. Bode plots and data fitting of blends with water and corrosion precursors after 5 h immersion. See the Table for blend composition

Again, at low frequencies the impedance values could not reach the plateau, therefore, Nyquist plots were further used as the means to calculate R_p (Fig. 5).

It must be noted that even in Nyquist plots the full semi-circles could be extrapolated only very approximately in quite many cases. Nevertheless, such extrapolation can still estimate

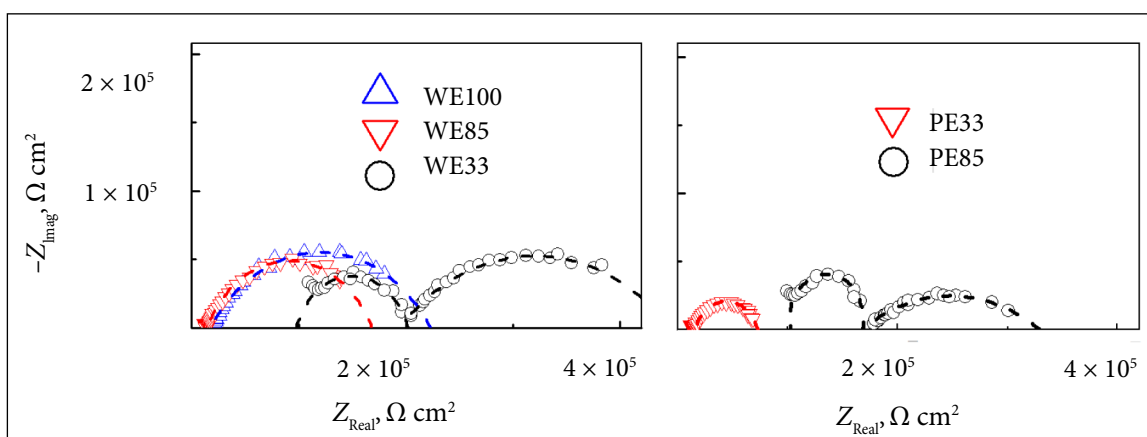


Fig. 5. Nyquist plots and data fitting of blends with water and corrosion precursors after 5 h immersion. See the Table for blend composition

R_p values [3]. This parameter is considered very important in describing the rate of corrosion processes and has been used by many researchers to investigate kinetics of steel corrosion in ethanol [14–15]. A number of replicates were run to assure that the R_p determination was repeatable. The EIS results appeared easily reproducible at least within the initial stages of steel surface exposure to the blends with or without water and corrosion precursors. Therefore, R_p changes with immersion duration were studied focusing on horizontally placed steel electrodes with the intention to relate the observed tendencies to possible corrosion mechanisms.

Influence of ageing on corrosion processes

As it could be anticipated, electrochemical characteristics of steel surfaces varied greatly with longer exposures to ethanol blends. The observations focused on R_p variation. Steel electrodes, immersed in the blends without water or precursors, showed major changes of R_p over the course of immersion (Fig. 6).

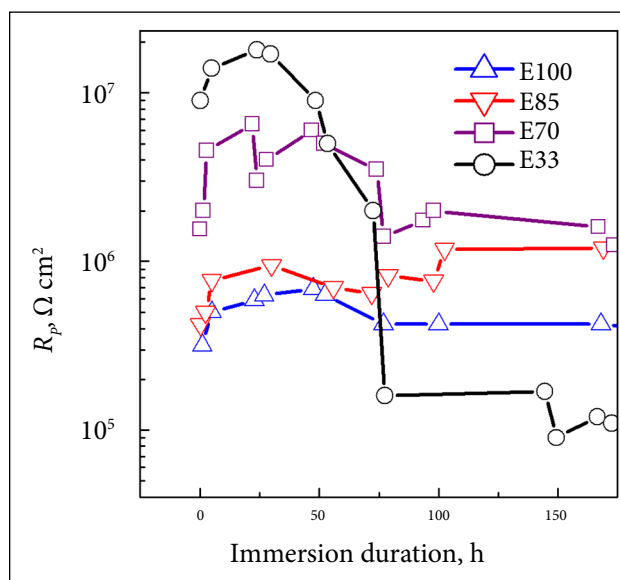


Fig. 6. Influence of ageing and hydrocarbon contents on polarization resistance of steel in blends with dehydrated ethanol

Initially, R_p would rapidly increase upon exposure to dehydrated ethanol blends with C7 hydrocarbons. After 24 h the R_p values started stabilizing and after some 50 h they attained a near-maximum value. This tendency was clearly expressed in all the blends and the immersion durations of the maximum R_p ranged from 40 to 60 h. Afterwards R_p of E100 and E85 still remained in the same vicinity, while E70 started decreasing with some major fluctuations. In agreement with Fig. 3 observations at 5 h immersion, the E85 behavior was again more different from E70 than from E100. The R_p drop in E33 was even more evident, supporting the trend that higher C7 contents led to more perturbations in electrochemical processes.

The magnitude of the R_p values was not less surprising. After longer immersions higher amounts of C7 did not give any advantage in terms of R_p values. It could be expected that higher proportion of C7 should lead to higher R_p , which was quite evident during the first 70 h of immersion. However, E70 and especially E33 demonstrated a significant drop in R_p after longer immersions.

Addition of water changed the R_p variation tendencies dramatically. Every blend demonstrated a rapid R_p drop immediately after immersion (Fig. 7). While R_p dropped and never recovered in WE100 and WE33, the tendencies in WE85 were more counter-intuitive. After dropping during the first 20 h or so, R_p did not change much for some time and then started increasing. After about 200 h immersion in WE85, it attained nearly the same value as the freshly exposed specimen, being

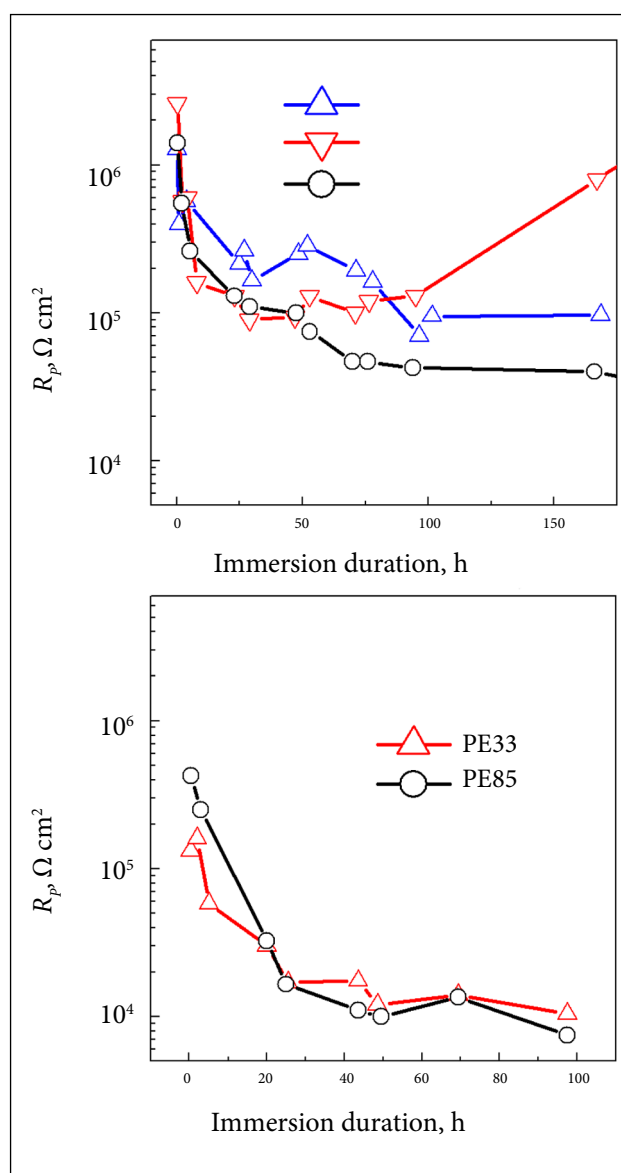


Fig. 7. Influence of ageing and hydrocarbon contents on polarization resistance of steel electrodes in blends with water and corrosion precursors. See the Table for blend composition

much higher than R_p of aged WE100 or WE33. Data from dehydrated blends was not in conflict with the R_p increase tendency of E85 either. Notably, the magnitude of R_p remained around $10^6 \Omega/\text{cm}^2$ both with WE85 and E85 during the most part, while the R_p change was much more dramatic within the other water-vs-dehydrated couples. These observations supported the perception that biofuels with 85% ethanol and 15% hydrocarbons might have better corrosion resistance than those with different ethanol-to-hydrocarbon ratios. However, it must be cautioned that except for water, above observations were made in blends without any other most widespread corrosion precursors. Therefore, these findings might not be easily extended to the technological or industrial environment.

Inclusion of corrosion precursors, i. e. 70 ppm acetic a. and 30 ppm NH_4Cl along with 5% water (all precursor concentrations are expressed per mass unit of dehydrated ethanol) affected R_p very significantly (Fig. 7). The major drop in the R_p magnitude was recorded in both blends with precursors and the gradual decrease continued far into the late stages of immersion. Some stabilization of R_p values around $10^4 \Omega/\text{cm}^2$ could be observed beyond 40 h of immersion. However, R_p values of PE85 were sharply lower than $10^6 \Omega/\text{cm}^2$, attained by WE85. This suggested that despite of 100 ppm concentration of precursors still meeting the bioethanol specification, their presence was crucial in terms of corrosion inhibition. Another notable observation was the similarity of R_p variation tendencies with immersion. Both PE85 and PE33 showed the same kinetic patterns: R_p went down rapidly during the first 20 h and then started stabilizing at around $10^4 \Omega/\text{cm}^2$. Tests with precursor-free blends showed major differences between E85 vs E33 or WE85 vs WE33. Therefore, nearly identical tendencies of R_p variation in PE85 vs PE33 confirmed that the precursor effects were very substantial.

Importance of acetic acid and chlorides on steel corrosion in ethanol was reported in many previous studies [10, 16, 17]. So it would be reasonable to extend the effects of corrosion precursors to ethanol-hydrocarbon blends. In many cases hydrocarbons could be viewed as relatively inert components without particular chemical reactions, which might interfere with corrosion mechanisms. The similarity of ageing effects on R_p of PE85 and PE33 implies that the importance of corrosion precursors outweighs the effects of hydrocarbon contents or water addition. It must be noted that the concentrations of acetic a. and chlorides were within the specifications for bioethanol fuels, while the amount of water exceeded the bioethanol specification limit (0.4% max) many times. Nevertheless, the influence of the precursors was much more significant in terms of the magnitude of the R_p value and their variation during the immersion.

Consequently, when technological implications are addressed, the presence of acetic a. and chlorides must be carefully considered. Obviously, water also affects corrosion kinetics to a large extent. However, as long as the specification limits are not exceeded, the electrochemical implications of water are not as significant as those of chlorides and acetic a.

Nevertheless, the presence of water introduces one more significant aspect. Its miscibility with ethanol-containing hydrocarbons might present a major problem [4–5]. When ethanol concentration is overwhelmingly large compared to hydrocarbons, water miscibility might not present an issue. But in this investigation the amounts of ethanol and hydrocarbons were quite similar in many samples. Therefore, in this study a more focused evaluation was performed to observe whether any phase separation might play a role in the corrosion process.

Observation of rust development and phase separation

With longer immersion durations the steel electrodes started getting some rust, which was clearly evident visually. When rust patterns expanded to cover a significant portion of the electrode surface, further electrochemical measurements were discontinued. Therefore, total immersion durations varied quite broadly for ethanol blends, as reflected in Figs. 6 and 7. One more factor was suspected as a contributor to rust formation. Since a number of refilling cycles (Fig. 1) were performed during the ageing studies, it was possible that H_2O could ingress from the environment into the blend due to a hygroscopic nature of dehydrated ethanol. Since the reference electrode contained chlorides, it was also possible that AgCl and especially LiCl could ingress through the electrode membrane into the electrolyte during the EIS measurement stage. It must be noted that the immersion of horizontal steel electrodes was performed separately from the reference electrode. Therefore, the contact of the electrolyte with the chloride-containing electrode was much shorter than the total immersion duration. Nevertheless, chloride ingress could have a significant effect on rust development as well.

The extent of water ingress into the electrolyte was studied separately. The steel electrode was held in a flask with C7 hydrocarbons for 50 days (i. e. 1 200 h) with a total of 10 refilling cycles. The refilling cycle was performed in the same manner as the EIS measurement, except that the steel electrode was not removed from the flask: C7 fluid was transferred into an electrolytic cell and exposed to the reference electrode for the same duration, as if it were an EIS measurement.

The C7 fluid was monitored for any phase separation. None could be observed for 50 days, although the steel electrode began rusting gradually (Fig. 8). Then after 50 days of storage a clearly defined water droplet was found on the surface of the steel electrode. Corrosion advanced much faster on the spot, which was covered by the water droplet. Since the original blend contained only C7 hydrocarbons without any ethanol, water was not expected to have any significant miscibility. Solubility of water in toluene and n-heptane is approximately 330 ppm and 100 ppm, respectively, at 25 °C according to engineering databases. Therefore, even small amounts of water could form a separate phase in C7 hydrocarbons, as in most non-polar organic solvents. When the electrode was

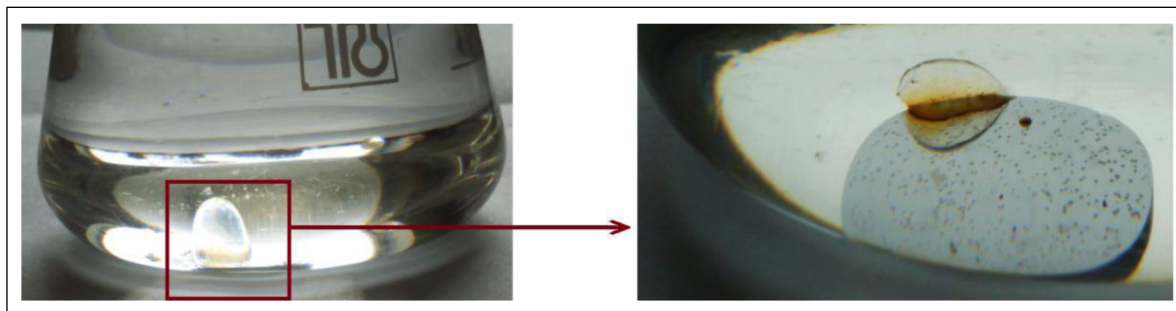


Fig. 8. Rusting of steel electrode in C7 hydrocarbons and formation of an aqueous phase as a result of water ingression

immersed horizontally into the C7 hydrocarbons, the water droplet formed not on the glass bottom, which was a bit lower than the electrode, but selectively on the steel surface. Steel is more hydrophilic than glass, therefore water molecules aggregate on steel surface much faster. Eventually, when the amount of aggregated water is large enough to engage surface tension forces, a droplet forms and remains attached to steel surface.

It must be noted that, if the electrodes were vertical, water droplets would be much more likely to roll off due to their higher density ($\sim 1 \text{ g/cm}^3$) than ethanol ($\sim 0.79 \text{ g/cm}^3$), n-heptane (0.68 g/cm^3) or toluene (0.87 g/cm^3). Horizontal surfaces are much more favourable for the water phase to accumulate. Also, if any chlorides were present in the ethanol/hydrocarbon blend, very likely they would pass into the water phase and further accelerate the rust formation. In this study, chloride ingression is quite probable due to the exposure of the blends to the reference electrode. Therefore, the rate of corrosion is much faster under water droplets compared to the remaining area of steel surface.

Since it is evident that water can become available even in hydrocarbon media, appearance of small rust spots on the electrodes can be explained even without any formation of a visually evident water droplet. Corrosion-related processes have been previously detected in films of hydrophobic liquids [18]. Adsorption of water molecules on steel leads to water-rich aggregates, which can engage into electrochemical corrosion mechanisms even within the non-conductive media, such as C7 hydrocarbons. Consequently, rusting can begin earlier than the actual phase separation, especially in presence of chlorides. Their presence may lead to yet another effect, the so-called “salting out” of the water phase. Water might be soluble in ethanol–hydrocarbon blends. But when chlorides or other salts are introduced, the ionic strength of the phase “chloride–water” is much higher than that of “water–ethanol”. As a result, water forms a separate phase much easier if the salts are present.

It can be summarized that two main factors explain why higher hydrocarbon contents in ethanol fuels increase the risk of corrosion, compared to fuels with 15% hydrocarbons or less. The first factor is the transformation of corrosion mechanisms in the interval of 15 to 30% amount of hydrocarbons, as evident by comparing E85 with E70 or E33 as well as WE85 and WE33. The second factor is the aqueous phase formation,

which can happen easier with higher hydrocarbon contents. Both factors become even more significant if chlorides and other corrosion precursors become available. This is usually the case in industrial or technological settings because current bioethanol specifications permit 70 ppm of acetic acid and 20 ppm of chlorides. Therefore, a great care must be exercised to prevent corrosion in case bioethanol fuels have more than 15% hydrocarbons.

CONCLUSIONS

1. Electrochemical properties of ethanol blends with 15% or less of toluene + heptane are similar to those of pure ethanol due to relative chemical inertness of hydrocarbons.
2. Further increase in hydrocarbon contents leads to major changes in corrosion kinetics, possibly due to solvation effects.
3. Aggregation of water into a separate phase can take place with higher amounts of hydrocarbons. Water droplets preferentially form on horizontal metal surfaces and promote rapid corrosion.
4. The presence of chlorides and acetic a. even within the bioethanol specification limits has more influence on steel corrosion than amounts of water, which might exceed the specifications several times.

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References

1. H. Jafari, M. H. Idris, A. Ourdjini, H. Rahimi, B. Ghobadian, *Fuel*, **90**, 1181 (2011).
2. L. M. Baena, M. Gómez, J. A. Calderon, *Fuel*, **95**, 320 (2012).
3. Y. H. Yoo, I. J. Park, J. G. Kim, D. H. Kwak, W. S. Ji, *Fuel*, **90**, 1208 (2011).
4. R. French, P. Malone, *Fluid Phase Equilibr.*, **228–229**, 27 (2005).
5. L. Chen, P. Sun, S. Ding, S. Yang, *Fluid Phase Equilibr.*, **379**, 1 (2014).
6. J. K. Thompson, S. J. Pawel, D. F. Wilson, *Fuel*, **111**, 592 (2013).
7. N. Morgan, A. Smallbone, A. Bhave, M. Kraft, R. Cracknell, G. Kalghatgi, *Combust. Flame*, **157**, 1122 (2010).
8. Y. D. Liu, M. Jia, M. Z. Xie, B. Pang, *Energy Fuels*, **27**, 4899 (2013).
9. W. Wang, P. E. Jenkins, Zh. Ren, *Corrosion Sci.*, **53**, 845 (2011).
10. S. Lichušina, A. Ručinskienė, A. Grigučevičienė, S. Asadauskas, *Chemija*, **25**, 20 (2014).
11. N. Shridhar, K. Price, J. Buckingham, J. Dante, *Corrosion*, **62**, 687 (2006).
12. V. F. Lvovich, *Impedance Spectroscopy*, John Wiley & Sons, Inc., USA (2012).
13. J. P. de Souza, O. R. Mattos, L. Sathler, H. Takenouti, *Corrosion Sci.*, **27**, 1351 (1987).
14. G.-L. Song, M. Liu, *Corrosion Sci.*, **72**, 73 (2013).
15. Sh. M. Bhola, R. Bhola, L. Jain, B. Mishra, D. L. Olson, *J. Mater. Eng. Perform.*, **20**, 409 (2011).
16. X. Y. Lou, P. M. Singh, *Corrosion Sci.*, **52**, 2303 (2010).
17. J. Abel, S. Virtanen, *Corrosion Sci.* (2015), in print [<http://dx.doi.org/10.1016/j.corsci.2015.05.027>].
18. S. Asadauskas, A. Grigučevičienė, K. Leinartas, D. Bražinskienė, *Tribology Int.*, **44**, 557 (2011).

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BENZINO ANGLIAVANDENILIŲ ĮTAKA ELEKTROCHEMINIAMS PLIENO KOROZIJOS PROCESAMS ETANOLYJE

Santrauka

Nors korozijos mechanizmai etanolyje yra išsamiai išnagrinėti, jų išvados ne visada gali būti pritaikytos bioetanolio ir benzino mišiniams. Dėl vandens priemaišų gali vykti fazių atsiskyrimas ir prasidešti sparti korozija rezervuarų, vamzdynų ir kitų talpų dugne. Šiame tyrime atlikti elektrocheminiai eksperimentai įvertino korozijos mechanizmus ant horizontaliai įmerktų mažoanglio plieno elektrodų. Biodegalus imitavo elektrolitai su 100, 85, 70 ir 33 % (tūrio) dehidratuoto alkoholio kiekiais plus 1:1 n-heptano:tolueno mišiniai, taip pat įdedant vandens, acto rūgšties ir chloridų. Elektrodai buvo patalpinti horizontaliai į biodegalus ir periodiškai išimami matuojant elektrocheminio impedanso spektroskopijos parametrus. Korozija netikėtai paspartėjo didėjant angliavandenilių kiekiui, kaip spėjama, dėl dviejų veiksnių. Nors 15 % ir mažiau angliavandenilių turinčių elektrolitų elektrocheminė elgsena buvo panaši į gryną etanolį, koncentraciją pakėlus iki 30 % kinetika ženkliai pasikeitė. Antaras veiksnys siejasi su nedideliais vandens kiekiais, dėl kurių gali vykti fazių atsiskyrimas ir vandens lašelių formavimasis visų pirma ant horizontalių metalo paviršių. Fazių atsiskyrimas gali paspartėti ir dėl chloridų. Todėl jei angliavandenilių ir etanolio kiekiai biodegaluose yra panašūs, reikia labiau pasirūpinti apsauga nuo chloridų ir kitų korozijos pirmtakų.