

# Electrochemical corrosion studies of low-alloyed carbon steel in acidic methyl imidazolium derivate ionic liquids with varying water content

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## **ABSTRACT**

The application of ionic liquids (ILs) in a wide range of technologies requires a thorough evaluation of their corrosion behavior to typical structural steels. In this work, the corrosion effects of two acidic type methylimidazolium derivates (potential catalyst candidates) on a low-alloyed carbon steel were studied with electrochemical methods (potentiodynamic polarization and EIS). The ILs cause a moderate corrosion around 0.1 mm/year at water content up to 10% and severe corrosion around 1 mm/year at 100%, which underlines that before industrial applications of ILs systematic corrosion studies should be carried out as part of the process design. With both ILs we found that the cathodic process exhibited apparently good linear Tafel slopes in the cathodic polarization range but in the anodic range the IL with the hydrogensulfate anion showed an active-passive transition only at the highest water concentration. In this series at lower water concentrations, under 100%, a model assuming a potential-independent anodic current rate correctly matched with the polarization data. The EIS measurement data showed chaotic, but reproducible deviations in the low frequency range, which were interpreted as the effect of the timely variation of distribution parameters and they apparently did not affect the charge transfer parameters essentially.

**KEY WORDS:** *low alloy steel, passivity, kinetic parameters, EIS, polarization*

## **1 INTRODUCTION**

Conducting ionic liquids (ILs) have an increasing role in a number of research and industrial applications. They are used as conducting media in electrochemical systems [1, 2], replacing aqueous solutions. In high dilutions they can be used as corrosion inhibitors [3-9]. The corrosion inhibition effect of ILs, more specifically the effect of the organic chain length and the effect of water and oxygen on the corrosion rate, was studied by Molchan et al. [10]. In the hydrocarbon industry ILs are also applied as catalysts [11]. In other applications they serve as agents for polluting gas removal [12-14] or for biomass dissolving [15]. The reason of the application in some areas, e.g., in lithium battery developments [1, 2], is that most ILs do not contain dissociable hydrogen ion and thus the reactivity towards metals with strong reductive effect is greatly reduced. In other applications they appear as environmentally friendly solvents, although the earlier expectations are not met in some respect [16]. The applicability of acidic ILs instead of conventional inorganic or organic acids has been explored in reactions of industrial relevance [17], such as in alkylation [18] (e.g., in fuel production with high hydrogen content in their molecular structures [19]), biodiesel production [20] or oligomerization [21-23]. Brønsted acidic ILs, possessing dissociable protons either in the cation or the anion or both, showed high efficiency in these processes. Due to the acidic character, the industrial importance of these materials goes hand in hand with an increased corrosion risk and this fact justifies the study of the corrosion properties of such systems with varying water content.

Although ILs are used as corrosion inhibitors at very low concentration [7], it cannot be excluded that in higher concentrations or in pure form they are corrosive (as it happens with other types of inhibitors, too), therefore, in their usual applications it is essential to evaluate the corrosion

of the applied structure materials. In the past two decades a number of research papers were published on the corrosion properties of ILs in pure and diluted forms [5-9, 24]. The ILs are mostly molten salts, therefore ionically conductive which raises the possibility of corrosion processes on the metal-electrolyte interface. However, as many ILs do not contain dissociable hydrogen, therefore the usual corrosion mechanism, compensated by the reduction of the hydrogen ion, cannot take place in totally water-free IL media. In spite of this, small amounts of water can induce the corrosion process and, taking into account the possible compensating corrosion inhibitive effects of some ILs, the net effect of water contained by IL media cannot be predicted without experimental investigations.

In the present work, we focused on the corrosion behavior of a low-alloyed carbon steel in two imidazolium derivatives, 1-(4-sulfobutyl)-3-methylimidazolium trifluoromethanesulfonate (BHSO<sub>3</sub>-MIM-CF<sub>3</sub>SO<sub>3</sub>) and 1-(4-sulfobutyl)-3-methylimidazolium hydrogensulfate (BHSO<sub>3</sub>-MIM-HSO<sub>4</sub>), containing a varying amount of water with electrochemical DC polarization and electrochemical impedance spectroscopy (EIS) methods. Owing to the inhibitive nature of the butylimidazolium part of the cation, BHSO<sub>3</sub>-MIM-HSO<sub>4</sub> was successfully tested earlier on mild steel as corrosion inhibitor [5, 9]. In spite of this, our initial assumption was that these ILs may have notable corrosiveness as the HSO<sub>3</sub> cation group and the hydrogensulfate anion have an acidic character, and also the trifluoromethanesulfonate anion can increase the corrosiveness through the fluorine atoms. These studies have practical importance for all industries where these ILs are applied or processed in low-alloyed carbon steel vessels. Surface analytical [10, 12, 25] and electrochemical polarization experiments [4, 13, 24, 25] were carried out on other types of imidazolium derivate ILs but similar studies have not been carried out on these chemicals. This fact underlines the necessity of such investigations as these two compounds are candidates for application as catalysts in the hydrocarbon industry.

In this field, one of the controversial issues is the phenomenon of passivity. In the corrosion literature the word passivity is used in two meanings, and in many cases these are not distinguished. The 'thermodynamic' passivity is in accordance with the definition of Pourbaix [26], who meant the formation of a protective oxide layer as passivity; the 'kinetic' concept of passivity is based on the observation that during anodic polarization the current increase stops at the primary passivation potential and the current decreases with further anodic polarization. In what follows, we apply the concept 'passivity' as cited from E. McCafferty [27]: 'Passivity is defined as the reduction in chemical or electrochemical activity of a metal due to the reaction of the metal with its environment so as to form a protective film on the metal surface. This definition does not indicate what properties constitute a "protective" film nor does this definition tell us anything about the nature of the "film" itself.' It is known that in low water content IL media the low-alloyed carbon steels can undergo passivation in the anodic polarization range [13, 24, 28]. A review of Dilasari [29] summarized the corrosion mechanisms of non-ferrous metals, showing numerous examples on active anodic dissolution, active-passive transition and spontaneous passivation. The review confirmed that the corrosion rate of the investigated metals increased significantly on the addition of water to the ILs. As the lack of oxygen and the small amount of water exclude the pathways of creating oxide layers, the self-assembled layers of the IL can be a possible origin of passivation. According to Kityk et al. [30] 'a passive state in the studied solvents is probably connected with the formation of hardly soluble iron compounds on the metal surface known as "saline" passivation'. A similar opinion is concluded by Abbott et al. [31].

Considering the lack of oxygen, the cathodic reaction is the reduction of hydrogen ion [32- 35]. In the investigated acidic type ILs the source of the hydrogen ions can be either the water or the mobile, dissociable hydrogen atoms of the organic cations (where such part exists at all). In either case, the hydrogen ion, adsorbed on the electrode surface, can exhibit similar kinetic behavior. We think that water traces, typically in the 100 ppm order of magnitude or over, can be the main source of the observed cathodic process and this is confirmed by the observation that the increase of water content increases also the rate of the hydrogen evolution process [33]. We found no reference stating that water can be completely removed from ILs. The role of water can be ultimately determined, however, only if absolute water-free IL batches are produced.

As the conductivity of ILs is moderate [16, 17], in all DC polarization experiments it is necessary to apply ohmic compensation or, at least, prove that the effect of the ohmic potential drop is negligible. The lack of this evaluation can cause a systematic error in the calculation of the

corrosion current density and, consequently, the corrosion rate. Therefore, we put the emphasis of carrying out a correct numerical ohmic drop compensation and also applied a new, enhanced method of analyzing the fit to the Butler-Volmer (BV) equation in order to determine whether the electrochemical reactions are governed by the charge transfer step. These methods are described in the Experimental section. The numerical ohmic drop compensation requires the knowledge of the accurate value of the solution resistance which can be obtained from EIS measurements. From the EIS data we also provide the value of the polarization resistance as an additional figure characterizing the kinetic of the corrosion process.

## **2 EXPERIMENTAL PROCEDURES**

The experiments were carried out with the two organic salts, BHSO<sub>3</sub>-MIM-CF<sub>3</sub>SO<sub>3</sub> and BHSO<sub>3</sub>-MIM-HSO<sub>4</sub>. The structures of the two compounds are shown in Figure 1.

### ***2.1 Preparation of the ILs***

All reagents were commercially available (1,4-butanediol (Merck), 1-methylimidazole (Acros), trifluoromethanesulfonic acid (TLC) sulfuric acid (Reanal), solvents (VWR)) and were used without further purification. 1,4-Butanediol (0.20 mol) was added slowly to 1-methylimidazole (0.20 mol) in 10 ml ethanol. The mixture was stirred at room temperature for 48 hours. Ethanol was removed in vacuum and the product was washed with toluene (three times, 20 ml each) and diethylether (twice, 20 ml each) to remove any unreacted starting material. 1-(4-sulfobutyl)-3-methylimidazolium betaine was obtained after evaporation of the volatiles in vacuum at 60°C (yield: 73%). A mixture of the betaine (0.10 mol) and the acid (trifluoromethanesulfonic acid or sulfuric acid) (0.10 mol) was stirred at 150°C for 5 h under argon atmosphere. After being allowed to cool to room temperature, the ionic liquids were washed repeatedly with toluene (three times, 10ml each) and diethylether three times, 10ml each) and dried in vacuum at 120°C (yield: 97-98%). Residual water was removed at 140 °C in a rotary evaporator connected to a vacuum pump. Water content of the ionic liquids was determined by a Mettler DL35 Karl Fischer Titrator using CombiTitrant 5 (Merck). Water concentration data are included in Table 1. NMR data of the products corresponded well to the previous reports [36, 37]. The purity of the products was checked by elemental analysis. The analysis of BHSO<sub>3</sub>-MIM-CF<sub>3</sub>SO<sub>3</sub> (C<sub>9</sub>H<sub>15</sub>F<sub>3</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, M=368.35 g/mol, theoretical contents: C=29.35%, H=4.10%, N=7.61%) found: C=29.10%, H=4.35%, N=7.41%. The analysis of BHSO<sub>3</sub>-MIM-HSO<sub>4</sub> (C<sub>8</sub>H<sub>16</sub>N<sub>2</sub>O<sub>7</sub>S<sub>2</sub>, M=316.35 g/mol, theoretical contents: C=30.37%, H=5.10%, N=8.86%) found: C=30.17%, H=5.32%, N=8.61%.

### ***2.2 Electrochemical measurements***

The investigated IL materials together with the applied water contents (denoted as ‘series’ and ‘system’ respectively) are summarized in Table 1. Note that ‘F’ and ‘S’ shortly identify the trifluoromethanesulfonate and hydrogensulfate anions respectively (the cations are identical). The water content of the electrolytes was adjusted by adding water droplets to the ILs with mass measurement. The adjusted water contents of the series are included in Table 1. Due to the high viscosity of the investigated ILs, the materials were heated up to 70±2°C, in order to mix with the added water and also for filling up an airtight electrochemical cell. Since the ILs are moisture sensitive, these preparations were made in a glove box under argon gas atmosphere.

The electrochemical cell was a specially designed microcell comprising approximately 1 cm<sup>3</sup> solution and having a working electrode with diameter of 6 mm, i.e., surface of 0.28 cm<sup>2</sup>, as shown in Figure 2. The material of the working electrode (WE) was low-alloyed structural steel DIN St 45.8 (see composition data in Table 2) and the counter (CE) and reference (RE) electrodes were a platinum disk and wire, respectively. The conventional reference electrodes include an aqueous junction, which can be a source of impurities, especially water. The platinum, as an alternative reference electrode, does not have a well-established potential value, therefore it is applied as a ‘quasi reference electrode’ [25, 38]. As the potential of the applied reference electrode is not comparable to conventional reference electrodes, the polarization, i.e., the deviation from the corrosion

potential is published throughout the paper instead of the electrode potential. The working electrode was abraded with emery papers of grade 400, 600, and 1000 mesh, degreased with 5% solution of Ferroclean 7136 degreaser at 50°C, washed with distilled water and ethanol, and dried under argon flow.

The electrochemical experiments included potentiodynamic polarization measurements both in the wide and narrow polarization ranges and EIS measurements. All electrochemical measurements were carried out with a METROHM AUTOLAB PGSTAT 302N type potentiostat and a NOVA 1.11 type software. In the potentiodynamic measurements the scan rate was 10 mV/min and the polarization was started in the negative range from -250 mV polarization from the corrosion potential and was carried out to +1600 mV. In case of the EIS measurements, the amplitude of the applied potential signal was 10 mV (i.e., 20 mV p-p). All spectra were taken in the 10 kHz – 10 mHz range and 10 frequency points were measured per decade, in logarithmically equidistant distribution.

### 2.3 Evaluation methods

The potentiodynamic measurements were evaluated by means of conventional and new methods [39, 40]. The ohmic resistance of the solution was calculated from the high frequency end of the EIS impedance data. This figure was used to calculate the ohmically compensated potential in all potentiodynamic measurements:  $E_{COMP} = E_{MEAS} - R_s J$ , where  $E_{COMP}$  is the compensated electrode potential,  $E_{MEAS}$  is the measured electrode potential,  $R_s$  is the specific solution resistance ([resistance \* area]) and  $J$  is the current density. All potential data of the potentiodynamic DC measurements are given as ohmically compensated, wherever applicable. The polarization resistance was determined from the potentiodynamic data by means of linear fitting from the points in the vicinity of the corrosion potential ( $\pm 10$ mV) current-potential curves. The corrosion current density values were calculated with three methods: (i) from the extrapolation of the Tafel slopes to the corrosion potential, (ii) from the QA and (iii) from the RQA methods. In a recent publication [40], a new and accurate quadratic approximation (model QA) was proposed for the determination of the Tafel slopes from the narrower polarization range:

$$\ln(R_p J/\eta) \approx A\eta + \eta^2 S^2/3!, \quad (1)$$

where  $J$  is the current density,  $\eta$  is the polarization (deviation from the corrosion potential),  $R_p$  is the experimentally determined polarization resistance (assessed either from a linear or from a quadratic fit in the very close vicinity of the corrosion potential) and  $A$  is the asymmetric and  $S$  is the symmetric parameter in the following transformation of the BV equation:

$$J = J_{corr} \exp[A\eta] \operatorname{sh}[S\eta]. \quad (2)$$

The validity of the approximation is limited to  $|S\eta| < 1$  and is acceptably accurate (within 1% error [40]) if  $|S\eta| < 1/2$ . The decadic anodic and cathodic Tafel slopes are obtained as  $b_{a,10} = \ln(10)/(S+A)$  and  $b_{c,10} = \ln(10)/(A-S)$ . Note that  $b_{c,10} < 0$ .

In parameter fitting it is always important to examine the validity limits and conditions of the applied model. If all considerations are correct then one can be confident that the completed fitting may be free of artefacts. In case of model QA the following conditions should apply if physically relevant parameters are to be determined:

C1: The fit should give a relatively small residual error.

C2: Equation (1) is an incomplete quadratic equation as it has no constant term. The assessed constant term should be small compared to the values fitted point set.

C3:  $|S| > |A|$ .

C4: The coefficient of the quadratic term should be positive.

Equation (1) seems to be an adequate tool for determining the Tafel slopes and qualifying measurement data if they obey the BV equation, but further quality assurance improvement can still be achieved by a transformation of Equation (2) and launching the reciprocal quadratic approximation model (model RQA)<sup>1</sup>, which is linear in  $1/\eta$ :

$$\ln(R_P J/\eta) / \eta^2 \approx A/\eta + S^2/3! \quad (3)$$

In Equation (3) obviously a quite different weighting of the points is implemented. If the determined parameters are (nearly) invariant to such a distinctive change of the weighting of the measurement points then this is a further indication of obtaining physically relevant parameters. In this representation the following conditions should be met:

C5. The parameters S and A are calculated from the intercept and the slope of a linear function. Anomalies, if any, are carried by the higher order (quadratic etc.) terms, but they must not be very significant compared to the contribution of the intercept and the linear term.

C6. The intercept should be positive.

C1 and C3 apply for Equation (3), too.

A further numerical analysis was applied in the case of the systems S0, S1% and S10% where the assumption was made that the anodic process was potential-independent. In this case, the cathodic current was calculated from the anodic limiting current and the measured current:

$$\lg(|J_C|) = \lg(J_{A,L} - J) = \lg(J_0) \eta/b_{c,10}, \quad (4)$$

where  $J_C$  is the calculated cathodic current,  $J_{A,L}$  is the anodic limiting current and J is the measured current. If the  $\lg(|J_C|)$  vs.  $\eta$  function is linear then the assumption is proven.

The EIS measurement data were evaluated with the methods developed and applied in a previous publication [39], where a dispersion-invariant model of measured EIS spectra was presented, providing an alternative interpretation of the distortions of the Nyquist curves (depressed semicircles) and the related electrochemical phenomena, determining the polarization resistance separated from the effects causing the depression of the semicircles and formation of the Constant Phase Element (CPE). Starting out of a specific model (equivalent circuit) we proposed a couple of transformations of the transfer (impedance) function which provided the 'principal admittance', which is, according to the applied model, equivalent to the reciprocal of the polarization resistance. One of the best transformations was Equation (14) in the cited paper [39], which is slightly simplified to give Equation (5) here:

$$Y_C' / Y_C'' = Y_{PR} / Y_C'' + K, \quad (5)$$

where  $Y_C'$  and  $Y_C''$  are real and imaginary parts of the ohmically compensated admittance,  $Y_{PR} = 1/R_P$  and K comprises a set of variables that give approximately a constant. Equation (5) is tested by means of a 'sliding fitting' procedure, comprising a frequency range of an order of magnitude in each fitting and accepting the parameters corresponding to the highest frequency (but under 1 kHz anyway) local maximum of the correlation coefficient.

The polarization resistance was assessed by means of the graphical method, too. The graphical method [39] applies those four impedance points that have the highest absolute values of the imaginary part of the impedance in the Nyquist curves. Fitting a quadratic polynomial on these

<sup>1</sup> Model RQA was not included in the referenced paper [40].

points and calculating the extremum point  $Z'_{\max}(Z'_{\max})$  of the curve by deriving the fitted curve the graphical polarization resistance  $R_{p,gr}$  is obtained as

$$R_{p,gr} = 2 * (Z'_{\max} - R_s), \quad (6)$$

where  $R_s$  is the solution resistance calculated from the points of the high frequency end of the spectrum.

No conventional evaluation (e.g., nonlinear equivalent circuit fitting) was carried out on the EIS measurement data, partly because, as it will be shown, some of the measurements exhibited hitherto unexperienced type of deviations that cannot be evaluated in any conventional method.

### **3 RESULTS AND DISCUSSION**

The results of the potentiodynamic measurements of series F are shown in Table 3 and the respective polarization curves are shown in Figure 3. The curves in Figure 3 show active-passive transitions during extensive anodic polarization up to 1600 mV. It is appearing that in the highest water concentration system (F100%) the currents are significantly higher than in the three lower water concentration ones, while in these three systems the cathodic polarization curves are almost similar, and the variation of the water concentration has only minor effect on the anodic currents, too. The kinetic passivity, i.e., the apparently blocked anodic process in the course of the anodic polarization, is generally attributed to transport limitations, which are due to compact layer building mechanism in all kinds of corrosion kinetic systems. Whether this transport limitation is due to oxide layer formation, like in aqueous systems, or is connected with the formation of hardly soluble iron compounds on the metal surface (known as “saline” passivation [30]), cannot be assessed on the basis of electrochemical kinetic studies only.

The typical Tafel region (within  $\pm 200$  mV polarization around the corrosion potential, Figure 3) is worth a closer look. In this range well-fitting Tafel-slopes are obtained in both directions and also the interceptions of the cathodic and the anodic curves are alike, determining well-defined corrosion currents, which indicate that most likely a charge transfer controlled corrosion process took place in all cases. The values of the cathodic decadic Tafel slopes vary between -117 and -132 mV for systems F0, F1% and F10% and is significantly greater (-152 mV) for system F100%. The anodic Tafel slopes are very high in the systems F0, F1% and F10% and is much lower in system F100% with the highest water content (67 mV, which is near to the usual anodic Tafel slope values found in aqueous systems [42]). Apparently, the variation of water content does not influence the current-potential relations at lower water concentrations and causes great increase of the currents at F100%. This is related to the increase of the conductivity (see the respective data in Table 1). The increase of corrosion rate with increasing water content was also reported by Uerdingen et al. [41].

A fitting of model QA to the measurement data of system F is shown in Figure 4. The respective fit parameters are included in the Figure and the calculated corrosion parameters (Tafel slopes and corrosion currents) are included in Table 3. According to the results, the conditions C1-C4 are fulfilled and the polarization curves of series F obey the BV equation.

The fitting of measurement data of series F to the RQA model is also shown in Figure 4. Based on the Figure, the measurement data satisfy all the applicable conditions and obey the BV equation according to the model RQA, too. The kinetic parameters calculated from the fittings are included in Table 3. The comparison of the cathodic and anodic Tafel slopes and the corrosion currents indicate that the corrosion parameters obtained with the models QA and RQA are very similar but they show great differences in some cases to the values obtained with the Tafel-extrapolation. These differences indicate that kinetic parameters may be quite different in the vicinity of the corrosion potential and in the Tafel-range, especially on the anodic side. The pooled average  $\pm$  standard deviation of the cathodic and anodic QA, RQA evaluations of the Tafel slopes of

the systems F0, F1% and F10% in Table 3 give  $-143 \pm 12$  and  $393 \pm 52$  mV, respectively. The same values calculated from the linear Tafel sections give  $-123 \pm 6$  and  $222 \pm 45$  mV. The difference between the QA, RQA and the Tafel slopes is significant, especially in the anodic case (compare  $393 \pm 52$  and  $222 \pm 45$ ). This difference emphasises the importance of the assessment of the Tafel slopes and, finally, the corrosion current from the potential range as narrow around the corrosion potential as possible. Interestingly, in the system F100% with the highest water concentration, the anodic Tafel slopes obtained with the three methods are very similar (66, 65 and 67 millivolts). This result suggests that the anodic reaction takes place via the same mechanism in the whole range of the active anodic dissolution.

The analogous evaluation was carried out on measurement data of series S, too. In Figure 5 the full range and Tafel range potentiodynamic polarization curves are shown. The general and the Tafel slope extrapolation related data are included in Table 4. The cathodic curves had linear Tafel sections similarly to series F and the fitting of the Tafel slopes resulted in similarly good correlation coefficients. In the systems S0, S1% and S10% the anodic part of the current vs. potential curves looked rather like limiting current shapes than a typical passivation curves (they had no current maximum). It is also conspicuous that the 'limiting current' fell in the range of the corrosion current, assessable from the extrapolation of the cathodic Tafel slopes to the corrosion potential, giving the impression that the anodic current was potential-independent in the whole polarization range. Assuming such a mechanism, i.e., the anodic limiting current  $J_{A,L} = const.$ , it follows from the BV equation that the expression of the cathodic current  $J_C$  can be calculated according to Equation (4).

The  $\lg(|J_C|)$  vs.  $\eta$  curves are shown in Figure 6 and in Table 4. It is assumed that the anodic current is constant in the investigated polarization range ( $\pm 40$  mV, approximately the same as applied for the QA, RQA evaluations) and equals to its value measured around 200-250 mV, in the point where the absolute value of the derivative of the current-potential function has a minimum. The linear fit of the obtained curves has correlation coefficients greater than 0.99, i.e., the linear relationship explains a huge part of the variance, with a slight quadratic contribution. This result is an indirect but strong evidence that the anodic current is really constant in the investigated polarization range of  $(-40 \dots +250$  mV) and also that in the polarization range of the Figure ( $\pm 40$  mV) the cathodic current obeys the BV equation. This means also that in the cathodic polarization range no oxide reduction step is observable, which implies that an oxide film formation in these systems is unlikely at these water concentrations. The corrosion current, calculated from the extrapolation of the Tafel slopes in Figure 5, are greater than those calculated from the intercept of the linear fittings of Figure 6 (compare the respective data in Table 4), in agreement with the observation that the curves in Figure 6 bend towards the greater Tafel slopes with increasing cathodic polarization. The corrosion currents obtained with the two methods show a varying match with a relative error between 5% and 50%, but the order of magnitude of the calculated corrosion current data is the same, indicating that the rate of the anodic process is independent of the potential in a wide potential range, which includes also a part of the cathodic polarization down to  $-40$  mV. This conclusion does not support the existence of any passive film formation that is in accordance with the findings of Dilasari [29] who did not find any passive layer on the electrode surface showing passive behavior during electrochemical polarization, stating that '...the lack of dissolved oxygen in RTIL systems also affects the corrosion mechanism of metals, generating consequently a different mechanism for passivation'.

System S100% is significantly different also in this series; the anodic currents are more than an order of magnitude higher than in the lower water content systems, in accordance with literature findings [10] reporting the increase of the corrosion rate with increasing water content. The more conventional passivation curve shape, owing to the significantly higher water content of 100 %, is more likely the result of an anodic oxidation process [10, 30]. In this system the anodic curve exhibits a linear Tafel-section *formally*, but the extreme low value of the slope (36 mV/decade) makes it unlikely to be a charge transfer controlled range.

The check of the applicability of the BV equation with models QA and RQA was carried out also for these series and the results are shown in Figure 7. A thorough check proves that none of the curves fulfils the conditions C1-C6 of the BV equation as follows: In the evaluation of model QA the systems S0, S1% and S10% violate condition C4. For system S0 this is not evident from a visual evaluation, therefore a quadratic fit was

applied and the second order term is found to be very small, but definitely negative. As for the condition C4, system S100% could be appropriate but it violates condition C2. According to the conditions of model RQA the systems S0 and S1% could be appropriate but system S10% and S100% violate condition C5. A quadratic or higher order fit could probably indicate violation of other conditions, too, but these statements are sufficient to declare that in series S none of the systems obeys the BV equation in the investigated potential range. This result is in agreement with the evaluation of the wide range polarization curves, discussed above. Not surprisingly, because the (nearly) constant anodic current, as assumed in Equation (4), means that  $A \sim S$  in Equation (2) for the systems S0, S1% and S10%, that is, the parameters of Equations (1) and (3) are strongly correlated. Both evaluations (QA+RQA and Equation (4)) confirm that the anodic process of this series does not follow charge transfer kinetics around the corrosion potential. Also, this conclusion demonstrates the value of the QA and RQA analyses. With conventional evaluation methods conclusions on the corrosion kinetics can be made only on the basis of the wide polarization range data. In this case: the linear sections of the cathodic polarization curves (Tafel sections in Figure 5) indicate a charge transfer controlled corrosion mechanism on the corrosion potential and the shape of the anodic polarization curve of S100% indicates an active-passive transition, which also does not contradict the conclusion of charge transfer kinetics (at the corrosion potential). Both conclusions are derived from the wide potential range data (minimum 200 mV).

The conventional evaluation methods are not appropriate in these systems. In the narrow potential range,  $\pm 40$  mV in our work, the following conventional methods are available: (i) linear polarization resistance fitting, which does not provide any information on the mechanism, (ii) polynomial fit (e.g., third order), which provides figures for the corrosion current and the cathodic and anodic slope in all cases, even if the current-potential relationship does not obey the BV equation and (iii) a **nonlinear** fitting of the BV equation, but this, applied for the very narrow potential range, would provide highly correlated parameters with enormous systematic errors. The QA, RQA evaluations can, on the contrary, tell unambiguously whether the polarization curves in the narrow potential range around the corrosion potential fit the BV equation (as it happened in the case of the series F) or not. The performance of the QA and RQA models is demonstrated in Figure 8, too. In series F the current-potential curves are re-calculated (and not fitted!) from the model parameters and the results coincide with the original measured data with a high accuracy. In series S the shapes of the measured curves are very similar to those obtained in series F and may lead to a conclusion that both series may follow the same charge-transfer controlled mechanism. Such a conclusion can be rejected by means of the QA, RQA models.

From the corrosion current data of Table 3 it is concluded that the technical corrosion rate of the investigated low-alloyed structural steels in these media is around 0.1 mm/year in systems F0-F10% and is almost ten times higher in system F100%. In series S the trends are approximately the same. Consequently, the corrosiveness of these ILs is moderate at lower water content but can be severe around 100%, in agreement with the findings of Dilasari et al. [29].

The EIS measurements provided also interesting results concerning the corrosion properties of the investigated ILs. The results were sorted into two categories, namely 'regular' and 'irregular'. The Bode and Nyquist plots of the regular data of series F and S are included in Figures 9 and 10. The irregular data are shown in Figure 11. The regular EIS spectra show clear depressed semicircles at the higher frequency range while under a certain 'threshold frequency' each spectra starts irregular deviations of minor extent. Threshold frequency is defined hereby as the frequency under which observable deviations from the regular 'depressed semicircle' behavior occur. The irregular data, namely the data of systems F1% and S100% are similar in the higher frequency range but under the threshold frequency the deviations are much more expressed and burst into a chaotic disorder. In the Nyquist graphs the irregular data are connected with lines to demonstrate the sequence of the points as function of the frequency. As we were uncertain about the nature of this disorder, 'kinetic collapse', we repeated the experiments and obtained approximately the same order of magnitude deviations at approximately the same threshold frequency. Although the measurement setup included a good quality potentiostat and all the other equipment were in reasonably good condition, we could reproduce the phenomenon (only approximately, of course, as it was inherently a stochastic one by nature). The deviations came up always in the low frequency range, where the electrochemical measuring devices are typically very



stable and reliable, thus we had no reason to discard these measurements as artefacts, but initially we did not have a plausible and convincingly accurate conventional model to interpret them.

We also applied the so-called graphical method for the determination of the polarization resistance, described in detail in [39] too, which utilizes the impedance points around the extremum of the imaginary part of the impedance as a function of the real part (Nyquist representation, Equation (6)) and compared the polarization resistance figures obtained in these two ways. The advantage of both the dispersion-invariant and the graphical methods is that they do not require the low frequency range points for the determination of the polarization resistance and therefore they seemed to be useful for the calculation of the polarization resistance (or the principal admittance) and comparison of parameters obtained from the regular and irregular measurement data. The results for the regular spectra, the regular (higher frequency) parts of the irregular spectra and also the evaluation results of the irregular impedance data via Equation (5) are included in Table 5. The determination of the polarization resistance data from the impedance data of the regular ranges ( $R_{p,calc,reg}$  in Table 5) according to the linear function of Equation (5) yielded a squared correlation coefficient around or over 0.999, practically all straight lines, so these are not presented in a diagram here. The data obtained from the irregular ranges of systems F1% and S100% are included in Table 5 ( $R_{p,calc,irr}$ ) and their assessment via Equation (5) is shown in Figure 12. In order to get a better view of the relations and errors, the obtained polarization resistance data are presented logarithmically in Figure 13. In this Figure, also the equivalence line and the linear fitting line (applied for the regular points only) are shown. In Table 5, the polarization resistance data obtained from the potentiodynamic current-potential data are also included. The coherent trend of the polarization resistance data as a function of the water content is clearly seen. Data at the highest water content suggest a similar and notable degree of corrosion with both ILs and this finding confirms the importance of the dissociable  $\text{HSO}_3$  group of the common cation in the corrosiveness of the ILs. The  $R_{p,DC}$  data show the same tendency as the EIS data, but with significant numerical differences.

From Figure 12 it can be concluded that the irregular data, which exhibit the stochastic pattern in the Nyquist representation, form more regular linear relationships in the transformation by Equation (5). As the transformation leading to Equation (5) was developed to separate the contribution of the reciprocal of the polarization resistance (the principal admittance) from the contribution of other factors, causing the dispersion of the admittance and the CPE, and this transformation led to the assessment of a well-defined admittance component emerging from the underlying ‘noise’, it is plausible to assume that the observed ‘kinetic collapse’ is more likely related to the factors affecting the extent of the dispersion, than to the factors determining the principal admittance.

From Figure 13 it can be concluded that the polarization resistance values, calculated from the regular impedance data via Equation (5), exhibit a good correlation ( $r^2 = 0.945$ ) with the same data obtained from the graphical evaluation, which proves that both procedures (the graphical method and Equation (5)) determine accurately the same physical quantity. This result confirms the interpretation of the irregular data, too. The polarization resistance values obtained from the irregular data are slightly different, but this means only that the process leading to the stochastic EIS pattern also changes the polarization resistance (i.e., the principal admittance). The mechanism of this process is still unclear. We believe that there may be a number of EIS data in research laboratories which exhibit the same stochastic pattern and have not been published. With this paper, we would like to encourage the publication of similar data and the evaluation via Equation (5) or similar transformations published in [39].

The solution resistance figures, obtained from the EIS data, show the same trend as the conductivity data in Table 1. Apparently, the water concentration affects significantly the conductivity at 100% only and it has practically no effect under this value. The low conductivity of ILs under dry conditions is attributed to ion pair formation in ILs [38]. The increase of water content and the degree of hydration can open new mechanisms and lead to the observed increase of corrosion rate in both ILs.

## 4 CONCLUSIONS

Two acidic organic ionic liquids were synthesized and tested for the electrochemical corrosion properties on low-alloyed carbon steel (DIN St 35.8) in pure state and with varying water concentrations. The electrochemical testing methods included potentiodynamic polarization and EIS measurements.

- ☒ The potentiodynamic polarization data measured in series F ( $\text{BHSO}_3\text{-MIM-CF}_3\text{SO}_3$ ) exhibited linear Tafel sections both in the cathodic and the anodic polarization range and upon further anodic polarization showed typical active-passive transition similar to that of low alloyed carbon steels in certain neutral media. The current did not change significantly in the three lower water concentration systems but was approximately an order of magnitude higher in the highest water concentration system (F100%). In series S ( $\text{BHSO}_3\text{-MIM-HSO}_4$ ) the cathodic polarization gave apparently good Tafel sections but the QA, RQA models proved that in the narrow polarization range ( $\pm 40$  mV) the systems did not follow the BV equation and it was proven that the anodic reaction was potential independent in a wide polarization range.
- ☒ The technical corrosion rate, calculated from the corrosion currents obtained with different methods, is estimated to be around 0.1 mm/year in the F0 – F10% systems and is roughly ten times higher, around 1 mm/year in the F100% system. In the  $\text{BHSO}_3\text{-MIM-HSO}_4$  (series S) electrolyte the corrosion rates are approximately doubled in comparison to the series F, which might be attributed to the dissociable  $\text{HSO}_4^-$ -anion and the resulting more acidic character of the molecule.
- ☒ In the EIS measurements the polarization resistance data of the regular spectra and the regular sections of the irregular spectra, determined with the recently published dispersion invariant equivalent circuit model, gave very good agreement with the graphical evaluation figures, which confirms that both methods calculate the same physical quantity. In the irregular spectra at low frequency a reproducible ‘kinetic collapse’ was observed, which seemed to be of a stochastic nature in the conventional representations, but gave a good fit and well-defined polarization resistance figures with the application of the dispersion invariant method. According to these measurements, too, the water content causes an intensive change between 10% and 100%, but under 10% the effect of water on the corrosion parameters is not significant.
- ☒ These results suggest that in industrial systems the corrosion of structural steels must be considered under the given conditions, especially at water content above 10%, and raises the requirement of thorough corrosion studies before every application of similar compounds. Further research is required to give a deeper interpretation of the observed phenomena and also it is important to try to find other systems with similar EIS behavior.

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## 7 **FIGURE CAPTIONS**

FIGURE 1. Structures of the tested electrolytes.

FIGURE 2. Cross section drawing of the electrochemical cell.

FIGURE 3. Full measured potential range (inset) and the narrower Tafel range of the potentiodynamic polarization curves of series F. The linear fitting of the Tafel sections had a quadratic correlation coefficient  $r^2 > 0.999$  in the selected ranges in all cases.

FIGURE 4. Fitting of series F potentiodynamic measurement data to model QA (above) and to model RQA (below).

FIGURE 5. Full measured potential range (inset) and the narrower Tafel-range of the potentiodynamic polarization curves of series S. The linear fitting of the Tafel-sections had a quadratic correlation coefficient  $r^2 > 0.999$  in all cases.

FIGURE 6. Cathodic currents of the systems S0, S1‰ and S10‰ calculated via the BV equation assuming that the anodic current is constant in the investigated potential range.

FIGURE 7. Fitting of series S measurement data to model QA (above) and to model RQA (below).

FIGURE 8. Current vs. potential curves of series F (above) and series S (below). In series F also the re-calculated current values are included.

FIGURE 9. Bode and Nyquist diagrams of the regular systems of series F.

FIGURE 10. Bode and Nyquist diagrams of the regular systems of series S.

FIGURE 11. Bode and Nyquist diagrams of the irregular systems F1‰ and S100‰.

FIGURE 12. Transformed admittance data and linear fittings according to Equation (5) of the irregular sections of the respective systems.

FIGURE 13. Logarithm of calculated polarization resistance values  $R_{p,calc,reg}$  and  $R_{p,calc,irr}$  plotted against graphically determined values  $R_{p,gr}$ . Note that the fitting uses only the regular data, but irregular data are also included.

## 8 TABLES

Table 1. Summary of the composition of the investigated systems. 1 millage (%) equals to 1000 ppm.

Series ID	IL material	System ID	Nominal (target) water content, ppm	Actual water content, ppm	Conductivity mS/cm
F	BHSO <sub>3</sub> -MIM-CF <sub>3</sub> SO <sub>3</sub>	F0	0	55	0.14
		F1‰	1000	720	0.15
		F10‰	10000	8110	0.12
		F100‰	100000	129600	6.37
S	BHSO <sub>3</sub> -MIM-HSO <sub>4</sub>	S0	0	210	0.17
		S1‰	1000	790	0.15
		S10‰	10000	8150	0.17
		S100‰	100000	85530	2.8

Table 2. DIN ST 45-8 steel composition

Element	C	Si	Mn	P	S
%	≤ 0.21	≤ 0.35	0.4 – 1.1	0.025	0.025

Table 3. Summary of parameters assessed from the potentiodynamic measurements in series F. The '10' in the indices refer to the decadic Tafel-slopes b (J is the current density).

Parameter	System ID			
	F0	F1‰	F10‰	F100‰
OCP*/mV	-298	-287	-256	-324
Rs** / Ωcm <sup>2</sup>	1250	1060	920	40
Tafel-extrapolation				
b <sub>c,10,Tafel</sub> / mV	-117	-121	-132	-153
J <sub>corr,Tafel,c</sub> / mA/cm <sup>2</sup>	0.00422	0.00594	0.00585	0.0624
b <sub>a,10,Tafel</sub> / mV	186	285	195	67
J <sub>corr,Tafel,a</sub> / mA/cm <sup>2</sup>	0.0031	0.00693	0.00472	0.0455
Corrosion rate*** / mm/y	0.043	0.075	0.062	0.635
QA evaluation parameters				
R <sub>p,QA</sub> / Ωcm <sup>2</sup>	6980	4720	5390	415
b <sub>c,10,QA</sub> / mV	-128	-152	-150	-110
b <sub>a,10,QA</sub> / mV	380	453	356	66
J <sub>corr,QA</sub> / mA/cm <sup>2</sup>	0.00594	0.0105	0.00850	0.0431
Corrosion rate / mm/y	0.069	0.123	0.099	0.504
RQA evaluation parameters				
b <sub>c,10,RQA</sub> / mV	-124	-154	-149	-107
b <sub>a,10,RQA</sub> / mV	341	475	355	65
J <sub>corr,RQA</sub> / mA/cm <sup>2</sup>	0.00564	0.0107	0.00847	0.0421
Corrosion rate / mm/y	0.066	0.125	0.099	0.493

\*Open Circuit Potential

\*\*Solution resistance calculated from EIS data

\*\*\*Averaged values calculated from the anodic and the cathodic corrosion current.

Table 4. Summary of parameters assessed from the potentiodynamic measurements in series S. The '10' in the indices refer to the decadic Tafel-slopes b (J is the current density).

Parameter	System ID			
	S0	S1‰	S10‰	S100‰
OCP*/mV	-544	-352	-459	-324
R <sub>s</sub> ** / Ωcm <sup>2</sup>	1620	1800	1570	196
Tafel-extrapolation				
b <sub>c,10,Tafel</sub> / mV	-206	-224	-205	-193
J <sub>corr,Tafel,c</sub> / mA/cm <sup>2</sup>	0.0129	0.0107	0.0122	0.0701
Corrosion rate / mm/y	0.151	0.125	0.143	0.820
Calculations via Equation (4)				
b <sub>c,10,Tafel</sub> / mV	-147	-130	-115	N/A
J <sub>corr,Tafel,c</sub> / mA/cm <sup>2</sup>	0.0193	0.0125	0.0129	
Corrosion rate / mm/y	0.226	0.146	0.151	
η (J <sub>A,L</sub> ) / mV***	225	250	245	

\*Open Circuit Potential

\*\*Solution resistance calculated from EIS data

\*\*\*Polarization value of the anodic limiting current assessment.

Table 5. Comparison of the regular and irregular polarization resistance values calculated via Equation (5) with graphically determined data.

System ID	R <sub>P,gr</sub> / Ωcm <sup>2</sup>	R <sub>P,calc,reg</sub> / Ωcm <sup>2</sup>	Frequency range* (Hz)	R <sub>P,calc,irr</sub> / Ωcm <sup>2</sup>	R <sub>P,DC</sub> ** / Ωcm <sup>2</sup>
F0	3010	3060	0.631-6.31	N/A	6980
F1‰-1	1380	1400	2.0-20.0	1100	4720
F1‰-2	1200	1180	0.158-1.58	2170	N/A
F10‰	1288	1260	0.158-1.58	N/A	5390
F100‰	431	464	0.398-3.98	N/A	415
S0	2440	2450	0.2-2.0	N/A	3310
S1‰	2450	1490	0.1-1.0	N/A	4100
S10‰	3730	3780	0.126-1.26	N/A	4490
S100‰-1	712	716	2.0-20.0	321	373
S100‰-2	507	509	1.58-15.8	418	N/A

\*Low and high frequency limits of evaluation

\*\*R<sub>P,DC</sub>: Polarization resistance data obtained from the measured potentiodynamic current-potential curves in Figure 8.