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Research Article

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Concentration-dependent corrosion inhibition with electrochemical energy conversion systems by a disubstituted aromatic: A comparison of methods

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Abstract: The suitability of three electrochemical methods commonly used for the assessment of efficiency of corrosion inhibitors in practical applications has been examined by a direct comparison of relevant results with an aromatic corrosion inhibitor as example. Discrepancies between results are discussed, practical approaches taking inherent weaknesses of the methods are indicated.

Keywords: corrosion; alloyed steel; aromatic inhibitor; Tafel-plot; electrochemical impedance measurements; linear polarization resistance

1 Introduction

Corrosion as a mostly electrochemical process can affect both active materials and construction materials in systems for electrochemical energy conversion and storage. It can cause lowered efficiency starting with self-discharge growing into decreased component performance up to system failure. Except for *e.g.* the rare case of a disposable, printable supercapacitor made entirely of biodegradable and mostly very environmentally compatible materials [1], metals and their alloys and composites are present in most of these systems. Corrosion inhibition or at least control is thus important for increased efficiency of these devices and extended service of safe operation. Various modes of corrosion control and inhibition are known and well-established [2–14]. The use of soluble inhibitors suppressing possibly the anodic metal dissolution and/or the corresponding cathodic reaction (most commonly dioxygen reduction or hydrogen evolution in acidic media) is particularly attractive in systems with circulating water-based liquids as coolants like in water-cooled battery or fuel cell packs.

Assessment of known as well as new inhibitors with the aim of identifying optimum concentrations is required. Because of the dominating contribution of electrochemical processes in the corrosion of metals, electrochemical methods are frequently used to determine required data [15, 16]. In such studies thermodynamic parameters (*i.e.* corrosion potential E_{corr}) and kinetic parameters (*i.e.* corrosion current I_{corr}, corrosion current density j_{corr}, rate of corrosion C_{R}) are frequently determined. In addition to the identification of best operating conditions for corrosion protection materials and methods, the corrosion susceptibility of a material, efficiency of a coating or a corrosion inhibitor, or the aggressiveness of a possibly corrosive environment can be verified.

Three standard electrochemical methods are frequently used to determine these thermodynamic parameters and kinetic parameters: Linear polarization resistance measurements LPR [17], electrochemical impedance measurements EIM[1] [18–22] and potentiodynamic polarization (scan) measurements (PPM, Tafel-evaluation, a generally accepted acronym has apparently not been established) [23]. LPR and EIM easily yield a resistance value called in a more general use of the term polarization resistance R_{pol}, which is equivalent to the corrosion resistance R_{corr} of the studied electrochemical interface. It is basically the slope of the current-potential curve at the electrode potential where the measurement was performed. Conversion of the charge transfer resistance R_{ct} (*i.e.* R_{corr}) obtained with EIM from

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[1] Habitually this method is called electrochemical impedance spectroscopy EIS, but because this method does not show typical features of a spectroscopy this presumably inappropriate term is not used here.

equivalent circuit evaluation [24] into a corrosion current I_{corr} (and also corrosion current density j_{corr}) is possible provided the stoichiometry of the corrosion reaction, in particular the number of electrons z transferred in the electrode reaction, is known. In case of a corroding iron electrode the most likely number of electrons transferred in the presumably dominating anodic corrosion reaction is two. In an exact consideration the same question must be asked for the cathodic reaction, this causes an uncertainty because of the complexities, in particular the various stoichiometries, of the cathode reduction of dioxygen. Slopes taken from the Tafel-evaluation are needed in case of LPR for this recalculation using the Stearn-Geary equation [25, 26]. To avoid these problems when comparing for example corrosion inhibitors as done in the present report a comparison of corrosion resistances R_{corr} may be applied.

In the third method Tafel-evaluation of potentiodynamic polarization scans yields quite reliably corrosion potentials E_{corr} which may be valuable in judging corroding systems from a thermodynamic point of view. They can be compared also with E_{oc} measured as a function of time after assembly of the electrochemical measurement cell to verify whether enough time has passed to establish a stable E_{oc} and thus the corrosion potential E_{corr}. But determination of I_{corr} or j_{corr} from the Tafel-plot is not always as simple as demonstrated in textbook experiments [27]. Reviews in particular of DC-methods including critical assessments are available [28]. Critical comparisons of results of several methods, both electrochemical and non-electrochemical ones, in a research report appear to be the exemption but not the rule [27, 29, 30].

Although the three electrochemical methods presented above can be readily performed with current instrumentation which contains in terms of hard- and software all necessary features for the methods as well as the evaluation of data in the majority of reported studies only one method is used. Unfortunately the evaluation procedures sometimes lack transparency (in particular when done automatically as part of the used computer software), critical judgment of the reader is not supported; assessment of *e.g.* fits of EIM using equivalent circuits is not offered because of the absence of proper representations neither are Tafel-plots displayed.

In our previous studies [31] of disubstituted aromatic amines (nitroanilines, phenylenediamines, toluidines) and taking into account the well-known carcinogenicity of at least one ortho-substituted aromatic amine (*o*-toluidine [32, 33]) we have selected *o*-phenylenediamine (*o*-diaminobenzene) as the most effective inhibitor and as a sample a common mild steel (C45 according to EN, common designation 1.0503, for details see below) in contact with an acidic aqueous environment of 1 M HCl taking into account an overview of experimental methods including critical considerations of various methods [15].

2 Experimental

From commercially supplied steel C45 (standard composition 0.0 .. 0.42 wt% carbon, 0.00 .. 0.40 wt% silicon, 0.50 .. 0.80 wt% manganese, 0.00 .. 0.045 wt% phosphorus, 0.00 .. 0.045 wt% sulphur, 0.00 .. 0.040 chromium, rest to 100% iron) cylindrical samples with an exposed surface area of 1 cm^2 were cut and mounted to a holder cut from plexiglass. The sample surface examined later was polished with abrasive paper (wet paper, type 240, 320, 400, 600 and 1000) followed by a final polishing with an aqueous slurry of 13 μm particle size α-Al_2O_3 to a mirror-like appearance. The circumference of the cylindrical sample was covered with PTFE-tape. Between measurements polishing (mostly the last step only) was repeated when traces of corrosion products had appeared on the shiny surface. HCl (37%, VWR) was used as obtained to prepare a 1 M aqueous electrolyte solution. As inhibitor *o*-phenylenediamine (VEB Jenapharm Laborchemie Apolda) was used as received and added to the electrolyte solution at various concentrations. In a three-electrode H-cell a platinum sheet counter electrode (1 cm^2 size) and a saturated calomel reference electrode were used. All measurements were performed at room temperature and after a stable electrode potential value E_{oc} had been established (usually after a few minutes).

LPR and PPM measurements were performed on a potentiostat IVIUM COMPACTSTAT PLUS Electrochemical Interface at experimental conditions (scan rates 2 $\text{mV}\cdot\text{s}^{-1}$ and 50 $\text{mV}\cdot\text{s}^{-1}$, respectively) as recommended elsewhere [15]. EIM was performed at E_{oc} with a potentiostat Solartron SI 1287 connected to a frequency response analyzer SI 1255 interfaced to a PC in the frequency range 50 kHz to 1 Hz, with 10 data points per frequency decade at a sine wave amplitude of 5 mV. Measurements of impedance and E_{oc} were repeated five times per sample. For data handling, in particular for fitting of the obtained impedance data, Boukamp software (version 2.4) was used. A Randles-type equivalent circuit (Figure 1) was assumed as has been employed in previous studies reported by the present authors [34–36] with the constant phase element Q instead of a simple double layer capacitance taking into account the non-ideal capacitive behavior of the electrochemical double layer [37–41]; for a broader discussion see ref. [24]. All parameters of all equivalent circuit elements have been fitted, only the values of R_{ct} (i.e. the corrosion resistance R_{corr}) relevant for

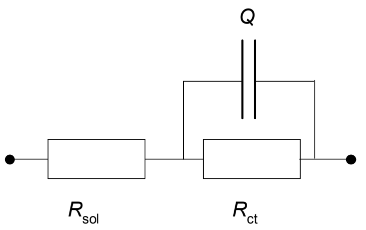

Figure 1: Equivalent circuit used in impedance measurements.

this comparative study are listed and discussed below. Averages of five or more measurements are reported, no further statistical treatment was applied.

3 Results and discussion

Typical plots of potentiodynamic polarization measurements of the steel sample in plain aqueous 1 M HCl solution and in a solution containing in addition *o*-phenylenediamine as an inhibitor are shown in Figure 2.

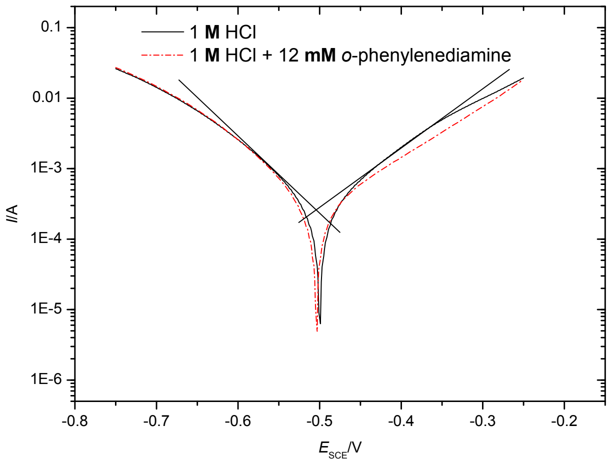

Figure 2: Tafel-plots of a C45 electrode in aqueous 1 M HCl solution without/with inhibitor 12 mM *o*-phenylenediamine.

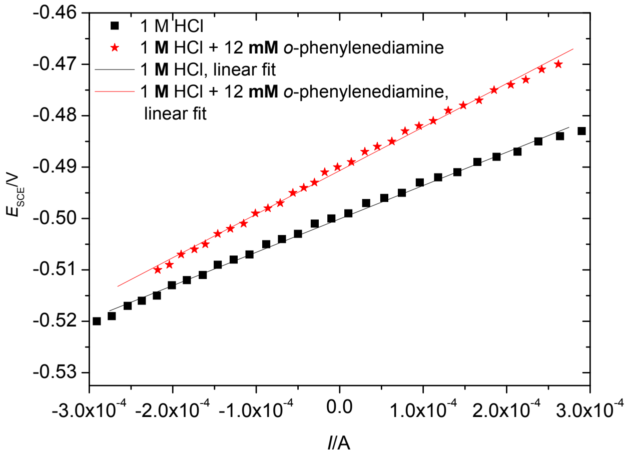

Figure 3: LPR plots of selected systems, for details see labels.

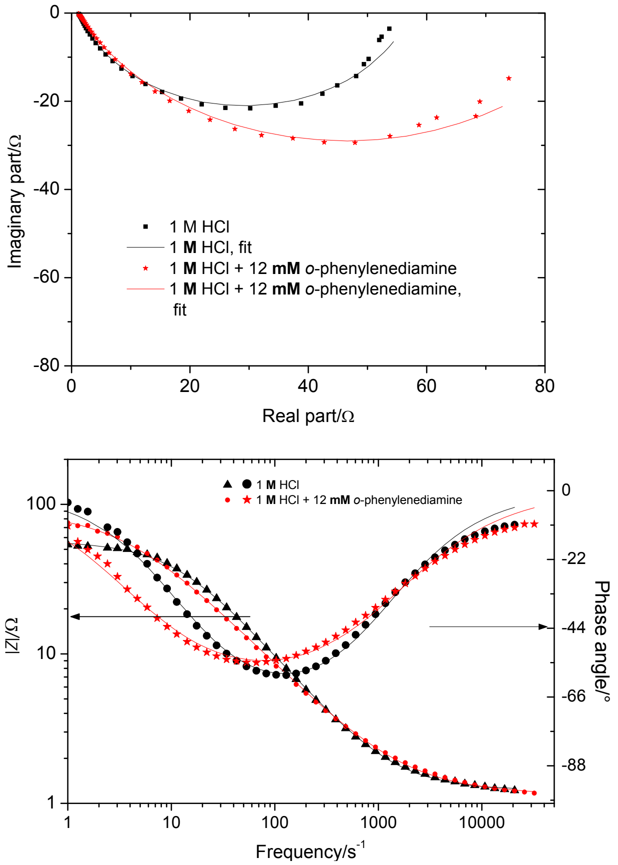

Figure 4: Results of impedance measurements (top: Nyquist plot, bottom: Bode plot); symbols: measured data, lines: fit and simulation.

As already addressed in passing in the introduction above determination of I_{corr} from the displayed plots is not as easy as suggested from synthetic plots assuming only charge transfer control (see for examples [15, 27]) and consequently showing straight lines at sufficiently large overpotentials η (in case of a two-electron process at $\eta >$ ± 59 mV the minor partial current drops to less than 1% of the major partial current). In the displayed plots at these sufficiently large overpotentials the plots are not linear at all. The lines shown in Figure 2 were placed at η = ± 59 mV and the intersections were used to find the value of I_{corr}. Results are collected in Table 1.

A plot of LPR data for two studied systems (the same as in Figure 2) is shown in Figure 3. Different from the uncer-

Table 1: Collected results for the studied systems

	System:	1 M HCl	1 M HCl + 2 mM *o*-phenylenediamine	1 M HCl + 7 mM *o*-phenylenediamine	1 M HCl + 12 mM *o*-phenylenediamine
Method	Parameter	-	-	-	-
E_{oc}	$E_{corr.\ vs\ SCE}/V$	−0.497	−0.497	−0.486	−0.486
	$E_{corr.\ vs\ SCE}/V$	−0.499	−0.508	−0.505	−0.503
PPM	I_{corr}/A	$2.6 \cdot 10^{-4}$	$2.8 \cdot 10^{-4}$	$2.2 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$
	R_{corr}/Ω	49	45	58	49
LPR	R_{corr}/Ω	65	60	79	84
EIM	R_{corr}/Ω	52	58	75	89

tainties discussed above for PPM the linear interpolations provide precise results. Results are also collected in Table 1.

Finally impedance results are shown in Figure 4 for the selected examples already used for the preceding DC-method measurements. The listed values of R_{corr} are the average of five measurements. Agreement between the other parameters in the runs required to fully define the equivalent circuit as shown in Figure 1 is good, because the data are not relevant here they are not listed.

Relevant results from the EIM are again collected in Table 1.

The values of E_{corr} recorded after they reached a stable value (after a few minutes) scatter without providing obvious evidence of a particular corrosion protection provided at any of the studied inhibitor concentrations. In particular a significant and systematic shift to positive values as expected for such action cannot be observed. This is in qualitative agreement with observations for these systems reported earlier [31], it also confirms the limited predictive value of E_{corr} regarding the performance of corrosion inhibitors stated elsewhere [36]. The same conclusion is reached when inspecting the values of E_{corr} taken from the Tafel-plots (for examples see Figure 3).

For reasons discussed above the present comparison of the methods and the inhibition efficiency at different inhibitor concentrations is based on the obtained values of R_{corr}. Values obtained from LPR and EIM agree quite well for all studied inhibitor concentrations. For the inclusion of results obtained with PPM from the respective Tafel-plots I_{corr} were taken and converted into R_{corr} taking into account the considerations critically discussed above. For all systems values of R_{corr} are significantly lower than those obtained with the other methods. This means, in turn, that evaluation of the Tafel-plots has yielded values of I_{corr} which appear to be too large in comparison. Values listed in Table 1 show in addition no systematic growth of R_{corr} with growing inhibitor concentration. This can be rationalized when taking into account the inherent problem of "real world" Tafel-plots already addressed: With growing overpotentials further contributions become relevant resulting in a non-ideal Tafel-plot negatively impacting the graphical evaluation. This has been addressed in previous reports [12, 28]. The particular reasons for the deviation of Tafel-plots from straight lines at higher overpotentials are not relevant here, only the consequences regarding the use of Tafel-plots alone for determination of kinetic data should be considered: Within a given system where presumably similar processes causing such non-linearity will operate the result of the non-ideality does not affect a rating of inhibition efficiency. In the present case with increasing concentration of *o*-phenylenediamine corrosion inhibition grows as expected confirming conclusions reported in our previous report [31] based on PPM only. Given the noticed experimental uncertainties the use of PPM only may be sufficient and seems to be appropriate only in case of studies where just relative effects (*e.g.* the differences between inhibitor concentrations of between structurally different inhibitor molecules) are of interest and were differences in corrosion currents can be reasonably deduced from changes in I_{corr}.

In case determination of corrosion currents which are of interest in studies where corrosion rates are needed the use of more than one method is recommended with particular attention to the pitfalls encountered when calculating I_{corr} from PPM data.

4 Conclusions

Corrosion resistance values obtained with LPR and EIM agree quite well, whereas those obtained with PPM differ significantly and even do not show the expected change with growing inhibitor concentration. For comparative studies a single method may be sufficient to asses the corrosion efficiency of an inhibitor, but in investigations wherein more than one experimental parameter is varied (*e.g.* comparisons between different metals and different inhibitors) verification by at least two methods is recommended. Based on the reported observations LPR and EIM are particularly useful.

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References

[1] Aeby X, Poulin A, Siqueira G, Hausmann MK, Nyström G. Fully 3D Printed and Disposable Paper Supercapacitors. Adv Mater. 2021;2021:2101328.
[2] Kaesche H. Die Korrosion der Metalle, 3rd ed., Springer-Verlag, Berlin 1990.
[3] Kaesche H. The corrosion of metals, Springer-Verlag, Berlin 2003.
[4] Kelly RG, Scully JR, Shoesmith DW, Buchheit RG. Electrochemical Techniques in Corrosion Science and Engineering, Marcel Dekker, New York 2003.
[5] Groysman A. Corrosion for Everybody, Springer, Dordrecht 2010.
[6] Roberg PR. Corrosion Engineering Principles and Practice, McGraw Hill, New York 2008.
[7] Uhlig's corrosion handbook (Revie RW, Uhlig HH Eds.), Wiley, New York 2000.
[8] Perez N. Electrochemistry and corrosion science, Kluwer Academic Publisher, New York 2004.
[9] Revie RW, Uhlig HH. Corrosion and Corrosion Control, John Wiley&Sons, Hoboken 2008.
[10] Roberge PR. Corrosion Basics: An Introduction, 2rd ed., NACE International, Houston 2006.
[11] APV-Corrosion Handbook. APV, Getzville 2008.
[12] Jones DA. Principles and Prevention of Corrosion, Prentice Hall, Upper Saddle River 1996.
[13] Roberge PR. Corrosion Inspection and Monitoring, John Wiley&Sons, Hoboken 2007.
[14] Talbot D, Talbot J. Corrosion science and technology, CRC Press, Boca Raton 1998.
[15] Xie X, Holze R. Experimental methods in corrosion research. ChemTexts. 2018;4:5.
[16] Xie X, Holze R. Experimentelle Methoden in der Korrosionsforschung. Bunsen-Magazin. 2018;20:100-117.
[17] Scully JR. Polarization resistance method for determination of instantaneous corrosion rates. Corrosion. 2000;56:199-217.
[18] Lasia A. Electrochemical Impedance Spectroscopy and its Applications. Springer, New York2014
[19] Yuan XZ, Song C, Wang H, Zhang J. Electrochemical Impedance Spectroscopy in PEM Fuel Cells. Springer, London 2010.
[20] Orazem ME, Tribollet B. Electrochemical Impedance Spectroscopy, 2nd edn. Wiley, Hoboken 2017
[21] Holze R. Electrode impedance measurements: A versatile tool for electrochemists. Bull Electrochem. 1994;10:56-67.
[22] Barsoukov E, Macdonald JR. Impedance Spectroscopy. WILEY-Interscience, Hoboken, USA 2005.
[23] Standard refernce test method for making potentiostatic and potentiodynamic anodic polarization measurements. ASTM Standard G5-94.
[24] Fu L, Qu Q, Holze R, Wu Y. A comment on the need to distinguish between cell and electrode impedances. J Solid State Electr. 2019;23:717-724.
[25] Stern M, Geary AL. Electrochemical Polarization I. A Theoretical Analysis of the Shape of Polarization Curves. J Electrochem Soc. 1957;105:56-63.
[26] Stern M. A Method For Determining Corrosion Rates from Linear Polarization Data. Corrosion. 1958;14:60-64.
[27] Holze R, Experimental Electrochemistry: A Laboratory Textbook, 2nd ed., VCH-Wiley, Weinheim 2019.
[28] Nagy Z. DC Electrochemical Techniques for the Measurement of Corrosion Rates in: Modern Aspects of Electrochemistry 25 (Bockris JO'M, Conway BE, White RE Eds.) Plenum Press, New York 1993, p. 135-190.
[29] Younis AA, Ensinger W, El-Sabbah MMB, Holze R. Corrosion protection of pure aluminium and aluminium alloy (AA7075) in salt solution with silane-based sol-gel coatings. Mater Corros. 2013;64:276-283.
[30] Younis AA, El-Sabbah MMB, Holze R. The effect of chloride concentration and pH on pitting corrosion of AA7075 aluminum alloy coated with phenyltrimethoxysilane. J Solid State Electr. 2012;16:1033-1040.
[31] Babu BR, Holze R. Corrosion and hydrogen permeation inhibition for mild steel in HCl by isomers of organic compounds. Brit Corr J. 2000;35:204-209.
[32] Richter E. Biomonitoring of human exposure to arylamines. Front Biosci. 2015;7:222-238.
[33] Nakano M, Shinagawa T, Eitaki Y, Omae K, Takeuchi A, Iwasawa S, Fukai K, Yoshioka N, Tanaka S. Risk of bladder cancer in male Japanese workers exposed to ortho-toluidine and other aromatic amines. Int Arch Occup Environm Health. 2021; https://doi.org/10.1007/s00420-021-01658-2
[34] Liu D, Xie X, Holze R. Corrosion stability of metallic materials in dentistry as studied with electrochemical impedance measurements. Int J Electrochem Sci. 2019;14:4074-4082.
[35] Liu D, Xie X, Roscher J, Holze R. A comparative study of the corrosion stability of dental amalgams with electrochemical

impedance measurements. Mater Corros. 2020;71:949-955.

[36] Roscher J, Holze R. Corrosion of nonprecious metal alloys in dentistry in the presence of common saliva additives. Mater Corros. 2021, DOI: 10.1002/maco.202112297.

[37] Göhr H. Über Beiträge einzelner Elektrodenprozesse zur Impedanz. Ber Bunsenges Phys Chem. 1981;85:274-280.

[38] Shi J, Sun W. Equivalent circuits fitting of electrochemical impedance spectroscopy for corrosion of reinforcing steel in concrete. Corr Sci Prot Technol. 2011;23:387-392.

[39] Katayama H. Surface and Interfacial Analysis Using Electrochemical Impedance Measurement. J Japan Inst Met. 2014;78:419-425.

[40] Talian SD, Bester-Rogac M, Dominko R. The physicochemical properties of a [DEME][TFSI] ionic liquid-based electrolyte and their influence on the performance of lithium-sulfur batteries. Electrochim Acta. 2017;252:147-153.

[41] Niya SMR, Hoorfa M. On a possible physical origin of the constant phase element. Electrochim Acta. 2016;188:98-102.