Alkali salts of amino acids as alkaline additives for neutralization of acidic corrosion inhibitors

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Abstract

Amino alcohols, typically derived from an oil-based value chain, are frequently used as alkaline additives for neutralization of acidic corrosion inhibitors in industrial metal working fluids. The criterions for selection of these additives have changed in the last decades and are nowadays not only performance driven, but influenced by ecological considerations, toxicity and regulatory standards. We present amino acids as functional, nontoxic, non-hazardous, non-volatile, chemically stable and cheap alkaline additives for common acidic corrosion inhibitors. The resulting mixtures have been evaluated for Co, Ni and Cu-leaching and were analyzed by chip-filter assay, potentiodynamic polarization measurements, electrochemical impedance measurements and gravimetry for corrosion protection of iron and steel in aqueous environment at slightly alkaline pH. Of several amino acids tested, Glu and Tau were found to synergistically interact with several acidic corrosion inhibitors of the carboxylic acid and the phosphonic acid type. Glu had a particularly positive impact on the protective properties of phosphonic acids with low hard water compatibility and served as an antiscalant. Tau had also a positive effect on the anticorrosive properties of several acidic corrosion inhibitors and lead to low levels of Co and Ni-leaching. Glu and Tau might thus serve as commercially and ecologically attractive substitutes for current alkaline additives to acidic corrosion inhibitors.

Introduction

In 2017, 2.4 billion liters of metalworking fluids (MWFs) were utilized worldwide (Najiha et al. 2016). It is estimated, that MWFs cause up to 16.9% of the production costs in the metal-processing industry (Lotierzo et al. 2016; Najiha et al. 2016). They play a significant role in processes like drilling, forming, grinding or cutting of metals in reducing friction between tool and workpiece and as coolants. MWFs are therefore crucial to avoid thermal damage of work pieces and reduce wear on the tool (Brinksmeier et al. 2015). On the other hand, many of their ingredients have had serious impact on the environment and the health of metal workers (Bay et al. 2010). Many efforts were therefore undertaken to develop safer and more environmentally friendly MWFs (Rudnick 2005; Umoren et al. 2019). Following the principles of green chemistry (Anastas and Kirchhoff 2002; Kümmerer 2007), some of the key aspects in this context are: elimination of hazardous chemicals, simplification of MWF composition and increased resource efficiency (currently, most ingredients are derived from mineral oil), including longer service life of tools and MWFs, reuse and recovery of MWFs (Bay et al. 2010; Brinksmeier et al. 2015). They can be divided in three groups according to their formulation: oil-based, water-based and emulsions (Byers and Byers 2017). Due to its high coefficient of heat transfer, aqueous MWFs are particularly attractive if good cooling properties are needed. However, the use of aqueous MWFs demands addition of corrosion inhibitors (CIs) to protect workpiece and tool. Next to several other additives such as extreme pressure additives, antiwear additives, antifoam additives, biocides and emulsifiers, CIs are thus major components of MWFs and account typically for about 1-5 wt%. Many CIs are carboxylic acids (Kuznetsov 2016) and phosphonic acids (Abohalkuma et al. 2016; Byers and Byers 2017; Spikes 2004). Because the pH of MWFs is typically slightly alkaline (pH = 8.0 - 9.5) to reduce corrosion and microbial load, acidic CIs

are neutralized with alkaline additives such as amines or amino alcohols of low molecular weight, which are often used in excess to buffer the pH in the desired slightly alkaline region (Sanyal 1981). Typical examples include 2-amino-2-methylpropanol (AMP), 1-aminopropan-2-ol (MIPA) and triethanolamine (TEA) (Fig. 1), which are all water soluble primary or tertiary amines (Bennett and Bennett 1984; Byers and Byers 2017; Lotierzo et al. 2016). Secondary amines tend to react with nitrogen oxides and nitrite to carcinogenic *N*-nitrosamines and are therefore not used in this context. In addition to their buffering capacity at favorable slightly alkaline pH values, vicinal amino alcohols have anticorrosive properties, which has been assigned to the formation of protective layers (Jamil et al. 2003; Welle et al. 1997). Most studies on anticorrosive properties of amines (and amino alcohols) have been performed in acidic media and are therefore hardly comparable to the situation in alkaline MWFs. However, some studies at alkaline pH values (mostly related to corrosion in concrete (Soylev and Richardson 2008)) have been performed and week anticorrosive properties for amino alcohols were reported, only when high concentrations of these compounds were applied (Ormellese et al. 2009; Vyrides et al. 2013). Besides, synergistic effects of amino alcohols on the anticorrosive efficacy of acidic CIs in MWFs have been reported in some cases (Kern and Landolt 2001; Ochoa et al. 2004). In other cases no synergistic effects were observed (Brenna et al. 2017). The chemical mechanism behind the corrosion protective synergistic effects of amino alcohols is not completely understood. It has been postulated, that alkaline additives act by creating active sites on the metal surface, by a fast interaction with hydrated iron oxide films and create thus favorable anchoring points for the stable immobilization of the acidic CIs through chemisorption (Felhősi et al. 2002; Kern and Landolt 2001; Ochoa et al. 2005). Additional reasons might include their influence on surface activity of the neutralized CIs by formation of salts and/or their chelating ability for dissolved metal cations.

Despite their common use many amino alcohols have major drawbacks. TEA, for example, has been linked to allergic contact dermatitis (Bruze et al. 1995; Chu and Sun 2001), seawater ecotoxicity (Libralato et al. 2010) and carcinogenic activity (Fiume et al. 2013). In addition, it is listed on the EU “Control List of Dual-Use Items in Annex I to Regulation (EC) No 428/2009” which entails further regulation and higher cost. In addition, some amino alcohols like AMP or MIPA are relatively volatile. Substitution of these compounds by less toxic and environmentally friendly alkaline additives would therefore be desirable. In this context, amino acids combine a number of favorable features. They are nontoxic (many are edible), non-hazardous, non-volatile, chemically stable and available at low cost in large tonnages often from bio renewables (Beerthuis et al. 2015). Amino acids have therefore been frequently used in the context of green chemistry (Shirini and Daneshvar 2016; Somorjai et al. 2009; Yang et al. 2016) and investigated as green acidic CIs (Verma et al. 2018). However, the anticorrosive properties of amino acids at alkaline pH values are limited (Ormellese et al. 2009) and only selected amino phosphonic acids are used commercially as antiscalants and CIs mostly in combination with zinc salts (Moschona et al. 2018). Anticorrosive properties of amino carboxylic acids in acidic media have also been found to be improved by addition of Lewis acids such as Zn^{2+} or surfactants (Mobin et al. 2017; Pech-Canul and Chi-Canul 1999; Zhang et al. 2016). To the best of our knowledge no attempts to use amino acids as alkaline additives for organic acidic CIs have been reported yet.

A closer look at the structures of amino (carboxylic) acids and amino alcohols in Scheme 1 reveals structural similarities and striking differences in acidities, which apply (although to different degrees) not only to amino carboxylic acids depicted but also to related derivatives such as amino sulfonic acids. As indicated by pK_a values, the most important difference of amino alcohols and amino acids is the higher acidity of the acid group compared to the alcohol group. Amino acids are therefore deprotonated at neutral pH and the resulting carboxylate salts will thus increase the conductivity of solutions compared to non-ionic alkaline additives. Similar to many vicinal amino alcohols, α-amino carboxylates are good chelate ligands for alloying metals, forming water-soluble metal complexes. They might thus be corrosive to certain metals and contribute to leaching of these metals into the solution. Although undesired in possible applications of amino acids in MWFs, the latter aspect has been used for cobalt leaching in battery recycling with glycinate (Nayaka et al. 2016).

In this study we describe the application of amino acid sodium salts as alkaline additives for selected CIs of the phosphonic acid and carboxylic acid type. Anticorrosive properties of the resulting mixtures were evaluated with a visual chip filter assay, electrochemical measurements and gravimetry in slightly alkaline media. In addition, we analyzed leaching properties of pure alkaline additives and their mixtures with acidic CIs for Co, Ni and Cu as important alloying metals.

Materials And Methods

Chemicals

Chemicals were purchased from Sigma-Aldrich in reagent grade and used as received. Amino acids were converted to their sodium salts through dissolution in water and addition of the appropriate equivalents NaOH, prior to use. Carboxyphosphonic acids **3** and **4** (Fig. 1) were synthesized according to a literature protocol (Ruf et al. 2022).

Chip-Filter-Test

Evaluation of the anti-corrosive properties of the substances for iron was carried out according to DIN 51360-02-A using the aqueous, solution of the acidic CIs and alkaline additive in either hardwater (20dGH: $CaCl_2$ 340 mg/L, $MgSO_4$ 60.0 mg/L) or 0.5% aqueous NaCl (pH 8.3 ± 0.5) at the appropriate concentration (Tables S2 + S3, see supporting information). 1.2 or 1.5 molar equivalents of the alkaline additive were added for each acidic proton in acidic CIs. As an example, carboxyphosphonic acid **3** contains 3 acidic protons and 3.6 or 4.5 eq of the alkaline additive were thus added. 2 mL of the appropriate test solution was incubated with 2.0 g of sieved grey cast iron turnings from Riegger Industriehandel GMBH for 2 h, before rinsing and visual scoring according to DIN 51360-02-A. For data see supporting information: Tables S2 + S3

Evaluation of metal leaching

The leaching properties of alkaline additives were evaluated by suspension of 225 mg of the appropriate metal-powder (Co: powder, < 150 µm, ≥ 99.9% trace metals basis from Sigma-Aldrich; Cu: powder, < 425 µm, 99.5% trace metals basis from Sigma-Aldrich; Ni: powder 100 mesh/ 99.9% from Chempur) in 15 mL of an aqueous solution of the appropriate alkaline additive (1wt%, amino acids were used as sodium salts) or a mixture of an acidic CI and sodium-6-aminohexanoate (Na-AHX) and heated under reflux for 24 hours. 1.5 eq Na-AHX were added for each acidic proton in acidic CIs. As an example, carboxyphosphonic acid **3** contains 3 acidic protons and 4.5 molar eq Na-AHX were thus added as alkaline additive. The resulting suspension was cooled to room temperature, filtered and the metal concentration in solution measured directly *via* flame atomic absorption spectroscopy (FAAS). Reported metal concentrations are mean values of triplicate measurements.

Electrochemistry

Quadratic S235JR steel slides (30 x 30 x 2 mm, obtained from Franz Krüppel GmbH & Co KG, ingredients according to DIN EN 10025-2: C = 0.17%, Mn = 1.40%, P = 0.035%, S = 0.035%, N = 0.012%, Cu = 0.55%) for the electrochemical assays were treated according to ASTM G1 C3.5 and cleaned in an ultrasonic bath (HCl 6 m; Urotropine 7 g/L) for 10 minutes and then dried in a nitrogen stream. Potentiodynamic polarization curves were measured with a Gamry ParaCell setup. The samples were used as a working electrode and were exposed to the electrolyte with an O-ring sealed opening with a diameter of 1 cm^2. The counter electrode was graphite and the reference electrode was Ag/AgCl in a 3 M KCl solution (SCE) which has a shift of + 210 mV compared with a standard hydrogen electrode (SHE). Open circuit measurements were taken over a time of 200 s. Impedance measurements were carried out using AC signals of a 10 mV potential perturbation and the scanning frequency range was 100 kHz to 0.01 Hz with 5 point/decade. The polarization scan was between − 100 mV and + 100 mV against the open circuit potential with a scan rate of 5 mV/s. The electrolyte was either hardwater (20dGH: $CaCl_2$ 340 mg/L, $MgSO_4$ 60.0 mg/L, conductivity at 25°C: 861 µS/cm) or NaCl-solution containing the CI and the appropriate alkaline additive (final pH 8.3 ± 0.5). The polarization measurement was performed after 24 h exposure at room temperature. Data were processed with the program *Gamry Echem Analyst* (Version 7.8.2). The percentage inhibition efficiency $\%IE_{corr}$ was calculated as follows:

$$IE_{corr} = \frac{I_{corr,uninhibited} - I_{corr,inhibited}}{I_{corr,uninhibited}} 100\%$$

with I_{corr} values from the uninhibited (hard water 20dGH, pH 7.9–8.8) and inhibited solutions, respectively. Corrosion rates were calculated according to literature (Groysman 2010).

Gravimetric corrosion test

Rectangular S235JR steel slides (30 x 10 x 3 mm, obtained from Rocholl GMBH, ingredients according to DIN EN 10025-2: C = 0.17%, Mn = 1.40%, P = 0.035%, S = 0.035%, N = 0.012%, Cu = 0.55%) were treated according to ASTM G1 C3.5 and cleaned in an ultrasonic bath (HCl 6 M; Urotropine 7 g/L) for 10 minutes

and then dried in a nitrogen stream. Afterwards, the steel slides were immersed in test solutions for 12 weeks at rt with regular substitution of evaporated water by addition of demineralized water. Test solutions were obtained by dissolving the appropriate acidic CI in 2% aqueous NaCl and addition of 1.5 eq alkaline additive for each acidic proton in acidic CIs. As an example, carboxyphosphonic acid **3** contains 3 acidic protons and 4.5 eq alkaline additive were thus added. The pH of the resulting test solutions was 8.3 ± 0.5. The corrosion rate C_R in µm/y was calculated as follows:

$$C_R = \frac{\Delta m}{A \cdot d \cdot t} 365 \cdot 10^9$$

with Δm = weight loss in g, A = 840 mm^2 (sample surface), d = 7940 kg/m^3 (density of steel) and t = 84 d (immersion time). Each experiment was performed in triplicate.

Results And Discussion

Amino acids have a number of desirable properties for use in formulation of MWFs. If used as alkali salts, they serve as mild bases and can thus be used to buffer the pH of common acidic CIs to values around 8–9 (just as the above-mentioned amino alcohols). Several derivatives are readily available in large tonnages at low cost. In addition, most amino acids are non-toxic, non-hazardous, non-volatile and chemically stable. Following these criteria, we selected a set of simple amino acids for evaluation as alkaline additives to aqueous MWFs. Within this set of amino acids, glycine (Gly) was chosen as the simplest, alanine (Ala) as an alkyl-substituted, arginine (Arg) and lysine (Lys) as basic, glutamate (Glu) as acidic, serine (Ser) and cysteine (Cys) as donor-substituted and histidine (His) as heteroaromatic proteinogenic amino acid. In addition, 6-amino hexanoic acid (AHX) as a non-proteinogenic higher homologue and taurine (Tau) as a α-amino sulfonic acid were also included. All amino acids were used in the form of their sodium salts.

Selection of amino acids via chip filter test

For a fast selection of the most promising combinations of amino acids with CIs, we performed a standard chip-filter-test on grey cast iron. The chip filter test according to DIN 51360-2 is a standard method used in industry for evaluation of anticorrosive properties of MWFs for iron. Briefly, a defined amount of sieved grey cast iron chips is placed on a round paper filter and submerged in a hard water solution of an acidic CI and an alkaline additive. After incubation for 2h at room temperature and subsequent washing of the filter, corrosion marks are visually detected and scored between 0 (no corrosion marks) and 4 (strong staining of the filter due to corrosion). This assay is operationally very simple and can be easily used for medium throughput screening. In addition, it is quite sensitive, due the large surface area and the high corrosivity of grey cast iron chips. However, the optical detection of staining is slightly subjective and misinterpretation according to staining that is not caused by corrosion is possible. The chip filter test was therefore used for a preselection of promising mixtures only. These were afterwards evaluated in more detail using electrochemical measurements and gravimetry. Tables with all corrosion scores obtained by chip filter assay are available in the supporting information (Tables

S2 and S3). As a benchmark system we used an aqueous solution of 1,3,5-triazine-2,4,6-triaminocaproic acid (**2**, 64 mmol/L corresponding to 3 wt%) with TEA (3.6 or 4.5 molar equivalents respectively) as an alkaline additive. This mixture is used successfully in several commercial MWFs for applications involving steel tools. It has a relatively low pH value of 7.4–7.8 and shows complete corrosion protection (score = 0) in the chip filter assay. In brief, the following observations were made: 1. Organic additives such as TEA are essential for the performance of acidic CIs. When TEA was substituted by NaOH as alkaline additive to CI **2**, a corrosion score of 4 was obtained although the pH of this mixture (pH = 10.3, suggesting improved alkaline corrosion protection) was significantly higher than that of TEA/**2** (pH = 7.4). 2. Among the amino acids tested sodium salts of Tau, Glu and AHX were as effective as TEA (scores = 0 at 3.6 molar equivalents) all others were less effective (scores = 1–4). 3. Corrosion scores for all amino acids tested were improved to 0–1 with a slight increase in concentration from 3.6 to 4.5 molar equivalents. 4. Amino acids are also compatible with acidic CIs other than **2**. We have tested three commercial CIs **1**, **2** and **5** containing 1–3 carbocyclic acid groups as well as two recently described carboxyphosphonic acids **3** and **4** (Ruf et al. 2022) and obtained perfect corrosion scores for combinations with sodium salts of Tau, Glu and AHX in all cases. 5. All amino acids gave perfectly clear and colorless solutions upon formulation with acidic CIs. However, after storage of 1 month at room temperature, the mixtures containing Met showed a yellow color, indicating oxidative degradation processes. 6. Several mixtures with Gly gave an untypical uniform color reaction on filter paper after incubation with grey cast chips lacking the normal contoured staining pattern of corroded iron chips (see supporting information, Fig. S4). We attributed this finding to the formation of colored water soluble Gly-complexes with alloying metals, which might have been formed as a consequence of Gly-mediated metal leaching from grey cast iron chips. Of all amino acids tested Tau, Glu and AHX showed the most promising properties and were selected for further evaluation by electrochemical measurements.

Leaching properties of amino acids for Co, Ni and Cu

Leaching of alloying metals is an undesired property of MWFs. Cobalt leaching, for example, causes increased wear of tools and is a serious environmental and health hazard (Barceloux 1999). Given the observations made for Gly in the chip filter assay, we analyzed the leaching ability of several amino acids at slightly alkaline pH values. In addition, we evaluated selected mixtures with acidic CIs. As benchmarks we compared the leaching abilities of amino acids with TEA, AMP and MIPA. The latter two are marketed as low leaching additives for Co-containing alloys. In a first set of experiments, the appropriate metal powder was suspended with an aqueous solution of the alkaline additive and heated to reflux for 24h. Dissolved metal concentrations were measured *via* FAAS and are shown in Table 1.

The results confirm the low leaching capability of AMP and MIPA for Co and Ni (Table 1, entries 3–4). TEA in contrast leads to moderate concentrations of dissolved Co and Ni (Table 1, entry 2), which has been noted by other researchers before and attributed to the formation of water soluble TEA-complexes at least for Co (Zhang et al. 2010). For Cu, the trend is inverted and TEA leads to lower amounts of dissolved Cu than AMP and MIPA. Sodium glycinate on the other hand leads to exceptionally high levels of Co and Ni in solution and can thus be classified as a high leaching additive for these metals (Table 1, entry 5).

Leaching of Cu is moderate in this case. These findings are in accordance with the application of Gly as a Co-chelator for recycling of Co from lithium ion batteries (Nayaka et al. 2016). For comparison, we measured the leaching properties of *N*-methylglycine (Sarcosine, Sar, Table 1, entry 6) and *N*-dimethylglycine (DMG, Table 1, entry 7) and observed decreasing concentrations of dissolved Co and Ni with increasing steric demand of the Gly derivatives. Similar trends were observed with other proteinogenic amino acids (Table 1, entries 8–11): All amino acids tested with either increased steric hindrance through side chains at the α-carbon or the amino group are less corrosive to Co and Ni compared to Gly. It is of note, that a similar effect of sterically demanding sidechains is not observed for Cu-leaching. The leaching of Co and Ni is significantly increased for all amino carboxylic acids tested compared to amino alcohols like TEA, MIPA or AMP. The observed difference in leaching of Co and Ni versus Cu is reflected by the corresponding stability constants of amino carboxylic acid complexes with Co(II), Ni(II) and Cu(II) (Gergely et al. 1972). The reported complex stability constants reveal a small difference in stability for Gly complexes of Cu(II) compared to complexes with sterically more demanding α-amino acids. In contrast, significant differences in complex stability have been reported for Ni(II) and Co(II)-complexes of amino acids with different steric demand. For both metals, Gly-complexes were found to be the most stable. The observed dependence of complex stability from steric factors is most likely a consequence of a different complex geometry for Co(II), Ni(II) and Cu(II)-complexes. Amino acid complexes of Co(II) and Ni(II) have a 3:1-stoichiometry of ligand:metal with an octahedral coordination of the metal by three bidentate α-amino carboxylate ligands (Gu et al. 2007). Whereas amino acid complexes of Cu(II) have a 2:1-stoichiometry of ligand:Cu with a planar coordination of the metal by two bidentate α-amino carboxylate ligands (Casari et al. 2004). The latter planar arrangement is less crowded and therefore less sensitive to the steric impact of bulky side chains. Of all amino acids tested, Tau and AHX stand out with respect to their low corrosivity towards Co, Ni and Cu. While the α-amino sulfonic acid Tau (Table 1, entry 13) lead to concentrations of dissolved metal in the same range as the benchmark amino alcohol TEA, AHX as a mid-chain ω-amino carboxylic acid (Table 1, entry 12) leads to extremely low dissolved metal concentrations which were even lower than values obtained for the low leaching additives AMP and MIPA. Both non-proteinogenic amino acids show thus a drastically reduced corrosivity towards all three metals tested. Again, this decrease in corrosivity (and consequently improved leaching properties) can be explained with the corresponding complex chemistry as both Tau and AHX are less powerful chelate ligands compared to the proteinogenic α-amino acids mentioned before. We have also tested mixtures of various acidic CIs with AHX for leaching properties. All AHX combinations tested resulted in low concentrations of dissolved Co and Ni qualifying AHX as an excellent low leaching additive particularly for applications of MWFs with Co-hardened tools. Moderate corrosivity and accordingly higher concentrations of dissolved metal was observed for Cu only (Table 1, entries 14–18).

Table 1
Co, Ni and Cu-concentrations after extraction of the appropriate metal powder into aqueous test solutions after 24 h at reflux. Metal concentrations were measured as triplicate from the aqueous extracts via flame atomic absorption spectroscopy (FAAS) and are given as mean values

	additive[a]	pH	Co (mg/L)	Cu (mg/L)	Ni (mg/L)
1	NaOH	9.6	0.67	≤ 0.20	≤ 0.20
2	TEA	10.2	34.3	1.57	1.44
3	AMP	12.8	7.03	43.2	0.33
4	MIPA	12.6	0.82	26.4	1.32
5	Gly	9.6	2486	24.8	963
6	Sar	9.6	419	70.6	328
7	*N,N*-Dimethyl-Gly	9.6	207	154	75
8	Lys	10.8	501	109	166
9	Ser	9.6	592	0.33	231
10	Glu	9.4	454	86.0	192
11	Pro	9.6	438	239	318
12	AHX	10.1	≤ 0.20	0.81	≤ 0.20
13	Tau	8.7	34.4	5.76	8.92
14	**1**/AHX[d]	9.8	4.04	4.66	84.3
15	**2**/AHX[b]	9.8	3.76	5.53	53.3
16	**3**/AHX[b]	10.0	0.63	0.82	13.4
17	**4**/AHX[c]	9.9	0.72	0.70	152
18	**5**/AHX[b]	9.9	1.19	1.15	135

[a] Performed with 1wt% of the alkaline additive. Amino acids were used as sodium salts. [b] Performed with 3wt.% acidic CI and 4.5 molar equivalents AHX sodium salt. [c] Performed with 3wt.% acidic CI and 1.5 molar equivalents AHX sodium salt. [d] Performed with 3wt.% acidic CI and 3 molar equivalents AHX sodium salt.

Electrochemical evaluation of amino acids as alkaline additives

We started the electrochemical evaluation of amino acids in hard water (20 dGH) under the same conditions used for the chip filter assay mentioned above. Tricarboxylic acid **2** was chosen as acidic CI. The combination with TEA as an alkaline additive is an industrial benchmark system for corrosion

inhibition of iron and steel with high efficacy in hard water. Accordingly, we have not even been able to determine the limiting effective concentration of **2**/TEA in hard water by electrochemical methods and observed perfect protection even at low millimolar concentrations (Table 2, entry 3). Lower concentrations of **2** lead to too low conductivity of hardwater solution to obtain reproducible potentiodynamic results. Under the experimental settings chosen (hard water and S235JR-steel), the electrochemical evaluation is less sensitive to corrosion compared to the chip filter assay. An important difference is the relatively small and more homogenous surface area exposed to the corrosive media in the electrochemical setup, where a polished bulk metal serves as a working electrode. Even the lowest concentrations of the acidic CI **2** tested, were thus likely far above the limiting effective concentration for complete corrosion protection. The choice of alkaline additive has therefore almost no influence on the protective effect of CI **2** (at least during the measurement time span of 24 h). Even neutralization of CI **2** with NaOH lead to perfect corrosion inhibition (Table 2, entry 2). The same perfect anticorrosive effect was observed for the addition of sodium glutamate (Table 2, entry 4) confirming, that the use of glutamate as a substitute of TEA has at least no negative effect on the corrosion protection of CI **2**. More interesting was the influence of the alkaline additive on the carboxyphosphonic acid **3**. We have previously reported, that **3** is a less powerful CI in hard water solution than **2** and attributed this loss of performance to the low hard water compatibility of carboxyphosphonic acid **3** leading to precipitation of hardly soluble salts with di- and trivalent cations (Ruf et al. 2022). At concentrations significantly higher than carboxylic acid **2**, carboxyphosphonic acid **3** is thus less effective in corrosion protection of steel at least when neutralized with TEA (Table 2, entry 5). The time dependent OCP in Fig. 2A reveals a slow immobilization of **3** on steel accompanied by a steady decrease in potential, which is characteristic for the self-assembly of protective nanolayers by most amphiphilic phosphonic acids (Felhősi et al. 2002). However, after 16 hours, a rapid increase in value of potential is observed accounting for the partial degradation of the protecting layer on the metal surface. In parallel a milky suspension is formed indicating the precipitation of phosphonate salts. If TEA is substituted by sodium glutamate for neutralization of CI **3**, we observed a decrease in value of OCP over several hours down to a constant value indicating the formation of stable protective layers (Fig. 2A). The potentiodynamic curve reveals a pronounced anodic shift of the corrosion potential (Fig. 2B) corresponding to almost complete corrosion protection of steel in this case according to Tafel analysis (Table 2, entry 4). Electrochemical impedance measurements confirm these findings. Bode plots of electrochemical impedance measurements show the high anticorrosive efficiency of tricarboxylic acid **2** which is independent from the additives NaOH, TEA or Glu under the conditions employed. For carboxyphosphonic acid **3**, in contrast, the alkaline additive has an influence on the formation of protective layers and thus anticorrosive efficacy. The values of the Bode modules in the low frequency region are higher for **3**/Glu compared to **3**/TEA (Fig. 2C). The corresponding capacitive loop in the Nyquist plots is also larger (Fig. 2D). Both, high Bode moduli and large capacitive loops in Nyquist plots correlate with high corrosion resistance (Mansfeld 1990). We observed still a slightly milky suspension for **3**/Glu, however significantly less precipitate was formed (compared to **3**/TEA) suggesting that Glu improves the hard water compatibility of carboxyphosphonic acid **3** and serves as an antiscalant, similarly to other poly(carboxylic) acids (Jafar Mazumder 2020).

Table 2
Results of the potentiodynamic polarization measurements of S235JR-Steel after 24 h exposure against hardwater-solution (20 dGH, pH 8.3 ± 0.5) containing tricarbocxylic acid **2** or carboxyphosphonic acid **3** and various alkaline additives at room temperature

entry	CI, c (mmol/L)	additive	i_{corr} (nA/cm^2)	IE_{Icorr} (%)	E_{corr} (mV)	β_a (mV/dec)	β_c (mV/dec)	CR (µm/y)
1	-	NaOH[a]	37500	-	-584	544	1540	436
2	**2**, 2.2	NaOH[b]	43.8	99.89	-123	156	79.7	0.35
3	**2**, 2.2	TEA[b]	56.2	99.85	-141	184	76.9	0.65
4	**2**, 2.2	Glu[b]	12.5	99.97	-153	171	76.5	0.14
5	**3**, 18.8	TEA[b]	1790	95.23	-368	402	244	20.8
6	**3**, 18.8	Glu[b]	5.72	99.98	-142	186	61.5	0.15

[a] pH was adjusted with 1 M NaOH to 8.0; [b] 4.5 molar equivalents were used. Glu was used as disodium salt.

Although the observed antiscaling effect of Glu with carboxyphosphonic acid **3** in hard water was interesting to note, it was difficult to confirm the synergistic additive effects observed in the chip filter test on the corrosion protection of more powerful CIs in hard water. We changed the media therefore to more corrosive aqueous 0.5% NaCl solution. Carboxyphosphonic acids like **3** or **4** have been shown to have good corrosion protective properties in chloride containing media. Both compounds were therefore selected as acidic CIs and evaluated in combination with NaOH, TEA and different amino acid salts as alkaline additives. We determined the limiting effective concentrations of these combinations to achieve complete corrosion protection by potentiodynamic measurements and a selection of data is presented in Tables 3 and 4. The limiting effective concentration for **4**/NaOH was found to be around 30–35 mmol/L (Table 3, entries 2–4) for **3**/NaOH this value is slightly higher at 35–40 mmol/L (Table 4, entries 2–3). For carboxyphosponic acid **4**, the substitution of NaOH by TEA has a positive effect on the corrosion rate (Table 3 entries 5–6) lowering the effective limiting concentration to 20 mmol/L. No measurable effect has been seen for carboxyphosponic acid **3** and the limiting effective concentration remained at 35–40 mmol/L for **3**/TEA (Table 4, entries 4–5). The same trend was observed when amino acid salts were used as alkaline additives: For carboxyphosponic acid **3**, only Tau led to the same effective limiting concentration as NaOH. All other amino acid salts lead to a less effective corrosion protection with CI **3** and effective limiting concentrations between 60–70 mmol/L. The typical layer forming protective mechanism of amphiphilic phosphonic acids on steel is reflected by a steady decrease in OCP value over several hours as observed for **3**/NaOH (Fig. 4A). Similar time dependent OCPs were observed for **3**/Tau and with slightly higher values also for **3**/TEA. For **3**/AHX however, OCPs are significantly higher in value suggesting a less perfect layer formation. It is interesting to note, that the mixture of **3**/AHX has a significantly lower critical micelle concentration (cmc) of 1.7 mmol/L (measured by ^{1}H-NMR, see

supporting information, Table S1) compared to **3**/NaOH (30 mmol/L). Although not strictly comparable with the formation of protective monolayers on steel, this decreased cmc suggests a higher surface activity for **3**/AHX compared to **3**/NaOH which should come with better corrosion protection. The opposite effect was observed and other factors besides surface activity must be operating. Bode plots of electrochemical impedance measurements confirm the high efficiency of **3**/NaOH, **3**/TEA and **3**/Tau as layer-forming CIs, because the values of the Bode modules in the low-frequency region are highest for these three mixtures (Fig. 4C). Their capacitive loops in the Nyquist plots are also the largest among the mixtures tested (Fig. 4D). As mentioned above, both high Bode moduli and large capacitive loops in Nyquist plots correlate with high corrosion resistance (Mansfeld 1990). Bode plots of all mixtures including carboxyphosphonic acid **3** reveal only one time constant, suggesting charge-transfer-controlled corrosion processes (Macdonald 2005). A comparison with the second carboxyphosphonic acid **4** reveals a different influence of the alkaline additive. All amino acid additives lead to a significant decrease of limiting effective concentrations compared to **4**/NaOH. Again, AHX and also Gly were least effective and gave the highest limiting concentrations for the corresponding mixtures with **4**, whereas Tau and Glu had the best effect on corrosion protection of **4** and gave the lowest limiting concentrations (Table 3, entries 7–10). The corresponding time dependent OCPs (all measured at a concentration of 20 mmol/L for CI **4**) confirm the formation of protective layers with **4**/Tau, **4**/Glu and **4**/TEA with a regular decrease of OCP values within a few hours to a low constant value around − 100 to -200 mV. For **4**/AHX and **4**/NaOH significantly higher OCP values (-300 mV to -400 mV) were observed suggesting the formation of less perfect protective layers on steel. The potentiodynamic curves shown in Fig. 3B confirm the trend in efficacy for the alkaline additives tested and their pronounced influence on the anodic corrosion reaction. The noblest potentials and lowest current densities were observed for **4**/Tau and **4**/Glu followed by **4**/TEA, **4**/AHX and **4**/NaOH. The curves are significantly shifted in this series, suggesting a pronounced influence of the alkaline additive on the anticorrosive properties of **4**. We have again measured the influence of the additive on the cmc of **4** in water by ^{1}H-NMR, but observed only small differences ($cmc_{\mathbf{4}/NaOH}$ = 4.5 mmol/L, $cmc_{\mathbf{4}/TEA}$ = 4.7 mmol/L, $cmc_{\mathbf{4}/AHX}$= 7.8 mmol/L) which can again not account for the observed large differences in anticorrosive properties.

Table 3
Results of the potentiodynamic polarization measurements of S235JR steel after 24 h exposure to aqueous NaCl-solution (0.5wt.%, pH 8.3 ± 0.5) containing carboxyphosphonic acid **4** and various alkaline additives at room temperature

entry	4, (mmol/L)	additive	i_{corr} (nA/cm^2)	IE_{Icorr} (%)	E_{corr} (mV)	β_a (mV/dec)	β_c (mV/dec)	CR (µm /y)
1	-	NaOH[a]	26900	-	-511	136	144600	313
2	20	NaOH[a]	19200	28.62	-430	235	1020	223
3	30	NaOH[a]	536	98.01	-182	260	102	62.3
4	35	NaOH[a]	9.51	99.96	-153	251	79.1	0.111
5	15	TEA[b]	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]
6	20	TEA[b]	11.4	99.96	-190	382	37.9	0.134
7	15[a]	Glu[b]	14800	44.98	-458	193	460	167
8	20[a]	Glu[b]	7.59	99.97	-116	237	69.5	0.092
9	10[a]	Tau[b]	10800	59.85	-314	269	272	125
10	15[a]	Tau[b]	3.80	99.97	-115	173	68.0	0.044
11	25[a]	AHX[b]	3030	88.74	-413	344	166	35.2
12	30[a]	AHX[b]	27.4	99.90	-221	476	87.7	0.032
13	35[a]	AHX[b]	3.93	99.99	-113	177	67.7	0.046

[a] pH was adjusted with 1 M NaOH to 8.0; [b] 4.5 molar equivalents were used. Amino acids were used as sodium salts; [c] inconclusive Tafel-Plot due to extensive pitting corrosion.

Table 4
Results of the potentiodynamic polarization measurements of S235JR steel after 24 h exposure to aqueous NaCl-solution (0.5wt.%, pH 8.3 ± 0.5) containing carboxyphosphonic acid **3** and various alkaline additives at room temperature

entry	3, (mmol/L)	additive	i_{corr} (nA/cm^2)	IE_{Icorr} (%)	E_{corr} (mV)	β_a (mV/dec)	β_c (mV/dec)	CR (µm /y)
1	30	NaOH[a]	365	98.64	-296	978	93.5	4.18
2	35	NaOH[a]	364	98.65	-258	518	87.5	4.23
3	40	NaOH[a]	14.1	99.95	-164	183	71.7	0.164
4	35	TEA[b]	506	98.12	-581	38.9	106	5.88
5	40	TEA[b]	37.5	99.86	-240	263	68.2	0.436
6	30	Tau[b]	2650	90.15	-690	123	72.2	308
7	35	Tau[b]	253	99.06	-198	658	96.5	0.296
8	40	AHX[b]	1.420	94.57	-322	757	129	16.4
9	60	AHX[b]	1.470	94.54	-305	1270	146	17.1
10	70	AHX[b]	253	99.06	-297	802	115	11.1

[a] pH was adjusted with 1 M NaOH to 8.0; [b] 4.5 molar equivalents were used. Amino acids were used as sodium salts.

Gravimetric evaluation of anticorrosive properties

As noted previously, the performance of layer-forming CIs can be time-dependent. Since many industrial applications require efficient corrosion inhibition over longer periods than those measured with our electrochemical studies, we included a long-term gravimetric assay with rectangular steel slides (S235JR) of 30 × 10 × 3 mm size. 2% aqueous NaCl was used as media, sufficiently corrosive to provide a weight loss of 186 mg within 12 weeks of incubation at room temperature and constant pH ~ 8 (TEA/AcOH buffer) when no additional CI was added. This amounts to a corrosion rate of 121 µm/y (Fig. 5A). All CIs tested were compared to this value, and the corresponding reduction in corrosion is given in Fig. 5A (red bars, inhibitory efficiency, IE) next to the corrosion rates (blue bars). We have used the TEA/AcOH buffer as a reference system, because the pH is in the same range as in our test solutions, and AcOH is known to have almost no anticorrosive properties at neutral or slightly alkaline pH values on iron and steel (Hefter et al. 1997). We have previously reported, that **2**/TEA does not show good corrosion protection in chloride containing media (IE = 29%) whereas **3**/TEA is moderately effective (IE = 66%) and **4**/TEA is highly effective under these conditions (IE = 88%). The use of amino acid salts such as Glu instead of TEA improves the anticorrosive properties of **2** and **3** in NaCl solution significantly and leads to almost

perfect corrosion inhibition with **3**/Glu (IE = 92%). With **2**, corrosion is reduced to a less perfect (IE = 47%) but still improved value, when Glu was used as an alkaline additive instead of TEA. However, visual inspection of the test specimens after incubation in 2% aqueous NaCl for 72 weeks revealed almost polished metal surfaces for **2**/Glu (Fig. 5C), whereas large quantities of corrosion products were deposited for **2**/TEA (Fig. 5B). As noted above, Glu serves as an antiscalant preventing the deposition of corrosion products on the metal surface.

Conclusions

A set of proteinogenic and non-proteinogenic amino acids was evaluated for their potential as alkaline additives to acidic CIs for application in aqueous MWFs of slightly alkaline pH. Amino acids were employed as sodium salts and used for neutralization of common acidic CIs of the carboxylic acid and the phosphonic acid type. The resulting mixtures were analyzed with respect to Co, Ni and Cu leaching and anticorrosive properties for iron and steel. Major findings are:

1. All α-amino carboxylic acids lead to relatively strong leaching of alloying metals such as Co and Ni. An extraction assay revealed that Gly addition gave the highest concentrations of Co and Ni in solution. Leaching of Co and Ni decreases with increasing steric demand of substituents in α-amino carboxylic acids. However, all α-amino carboxylic acids tested lead to higher leaching of alloying metals than industrial low leaching amino alcohols like MIPA or AMP. The leaching properties of alkaline additives depend on the corresponding complex stabilities and Tau as well as AHX, which are both bad chelators, lead to low leaching of Co and Ni. Particularly AHX is an attractive low leaching additive leading to lower Co and Ni concentrations in solution than MIPA and AMP.

2. A visual chip filter assay of various mixtures of amino acids and acidic CIs revealed that many amino acids are compatible with CIs of the carboxylic and phosphonic acid type. Synergistic effects on the anticorrosive properties of CIs were observed for Met, Glu, Tau and AHX. However, Met was excluded from more detailed analyses, because of the limited chemical stability of the solutions.
3. Electrochemical evaluation of Glu, Tau and AHX as additives to a tricarboxylic acid (**2**) and two carboxyphosphonic acid (**3**) and (**4**) confirmed synergistic anticorrosive effects of Glu and Tau. Impedance measurements and time-dependent OCPs showed that Glu and Tau improve the layer-forming anticorrosive mechanism of the CIs tested. In addition, Glu improved the hard water compatibility of phosphonic acids such as **3**. Glu and Tau improved the anticorrosive properties of all CIs tested significantly and let to almost perfect corrosion inhibition at low millimolar concentrations of CIs even in corrosive media like 0.5wt.% aqueous NaCl. Mixtures of acidic CIs with Glu and Tau were found to be significantly more efficient than mixtures with the amino alcohol TEA.
4. The antiscaling activity and the synergistic anticorrosive effect of Glu was also confirmed by long term gravimetric tests on steel with carboxylic acid **2** and carboxyphosphonic acid **3**.
In summary, sodium salts of amino acids are valuable alkaline additives for neutralization of acidic CIs. Glu and Tau had a synergistic anticorrosive effect on several acidic corrosion inhibitors and were thus superior to common additives like TEA. Several amino acids have an added value, such as antiscaling

properties (Glu) or low leaching of Co and Ni (Tau and AHX). Amino acids may thus be used as economically and ecologically attractive substitutes for currently used amino alcohols.

Declarations

Patents

As a result of the work reported herein, a patent application has been filed: EP/2021/053871, “Amino acids as green neutralizing agents for acidic corrosion inhibitors”.

Supplementary Materials

The following supporting information can be downloaded at: XXXXXX, Overview of chemical structures for CIs and alkaline additives used in this work (Fig. S1); CMC evaluations by ^{1}H-NMR including experimental procedure, Table S1 and ^{1}H-NMR spectra (Fig. S2 and Fig. S3); chip filter test according to DIN 51360-2 including Tables S2 and S3 and Fig. S4; detailed view of Nyquist plots (Figure S5).

Author Contributions

Conceptualization, W.M.; methodology, W.M., E.R., T.N. and T.S.; validation, E.R., T.N. and T.S.; formal analysis and synthesis, E.R., T.N. and T.S.; investigation, E.R., T.N. and T.S.; data curation, W.M.; writing—original draft preparation, T.N. and T.S.; writing—review and editing, W.M., E.R., T.S. and H.K.; supervision, W.M.; project administration, W.M. and H.K.; funding acquisition, W.M. and H.K.; T.N. and T.S. contributed equally to this work. All authors have read and agreed to the published version of the manuscript.

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Conflict of Interest

The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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Scheme

Scheme 1 is available in the Supplementary Files section.

Figures

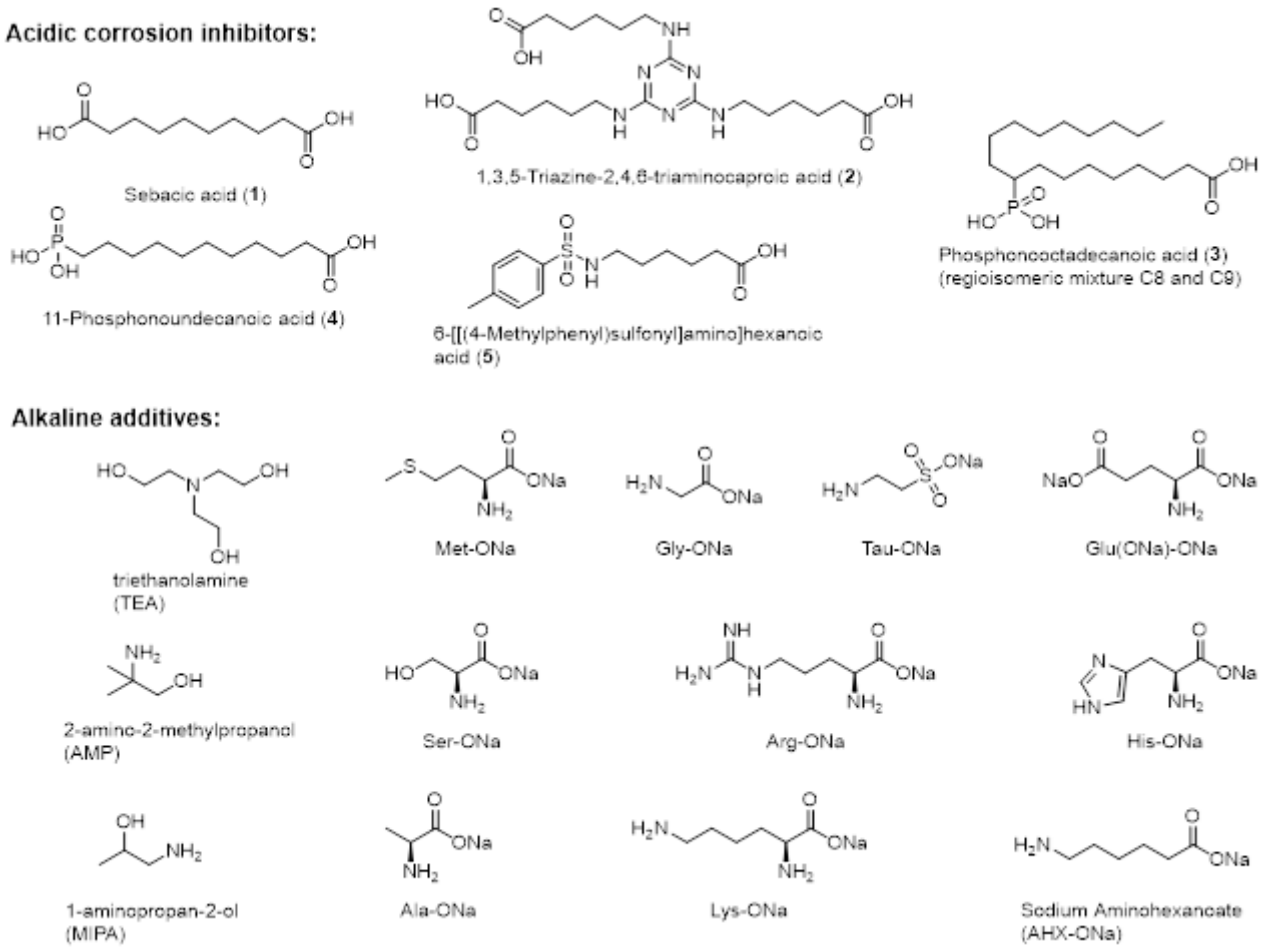

Figure 1

Chemical structures of acidic CIs and alkaline additives used in this work

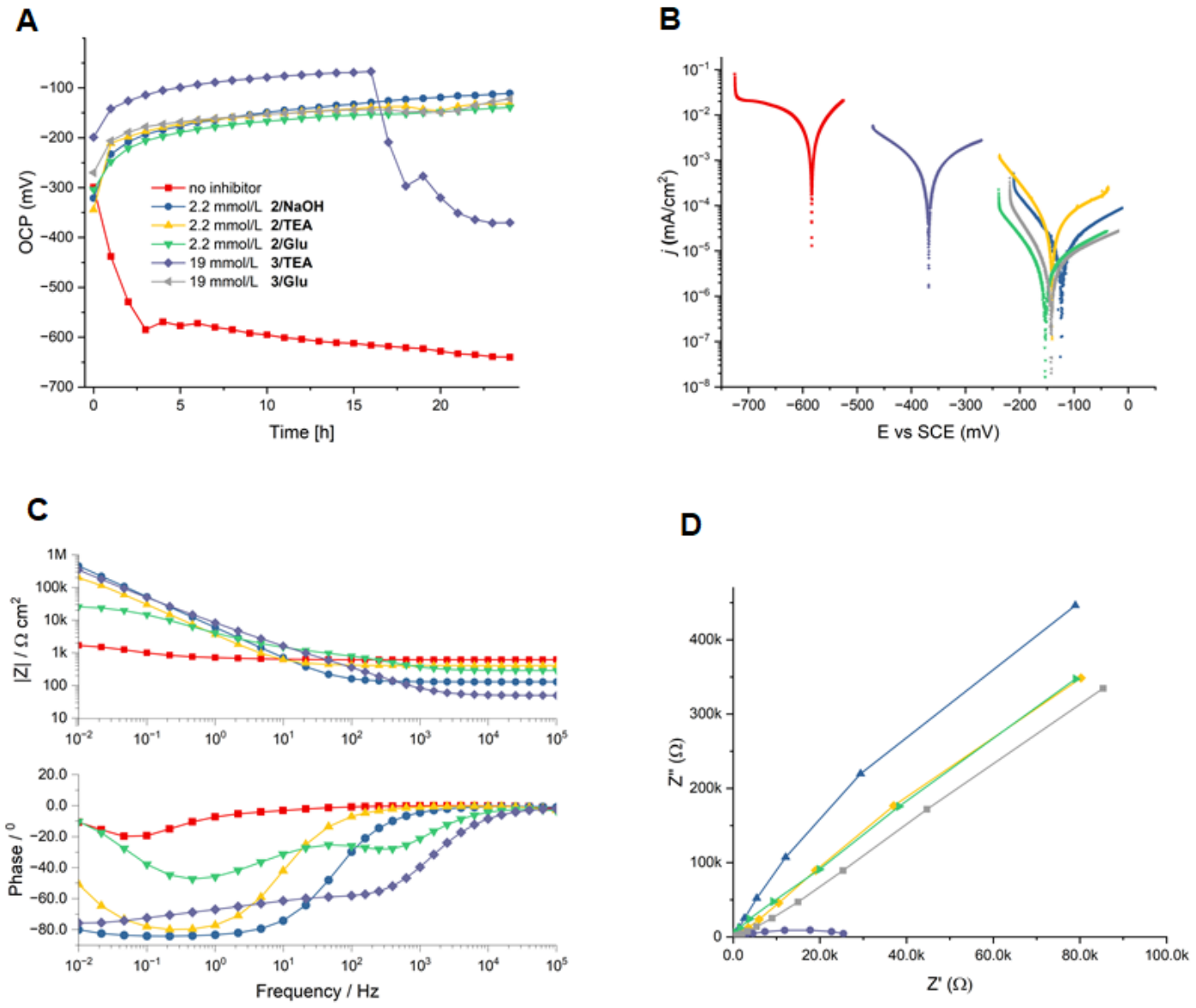

Figure 2

Electrochemical measurements of steel (SJR235) in hard water (20dGH, pH 8.3 ± 0.5) with tricarbocxylic acid **2** or carboxyphosphonic acid **3** and NaOH, TEA and Glu (disodium glutamate) as alkaline additives. A) Development of open circuit potential (OCP) with immersion time; B) potentiodynamic polarization curves after 24 h immersion; C) Bode plots of electrochemical impedance measurements. D) Nyquist plots of electrochemical impedance measurements

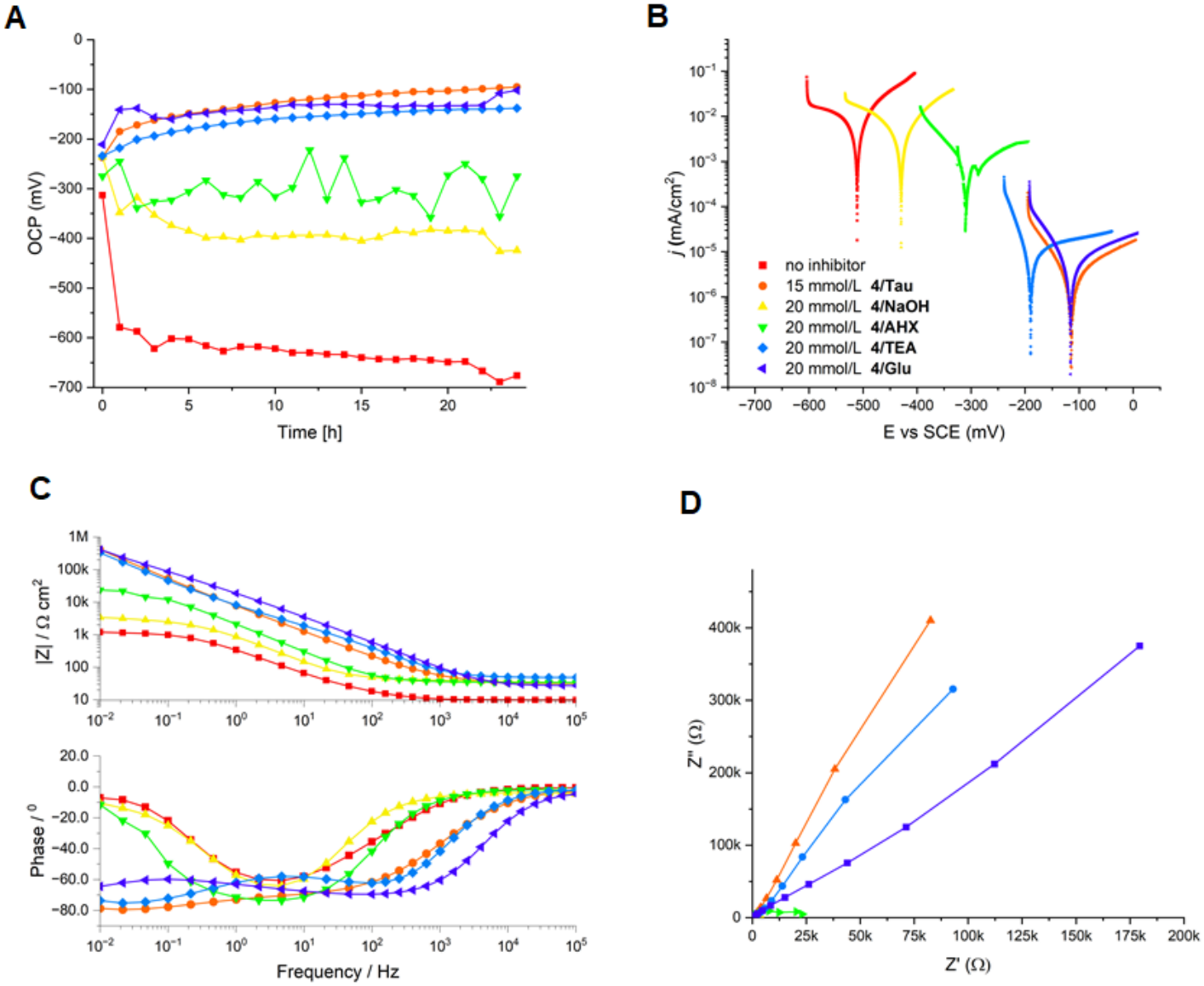

Figure 3

Electrochemical measurements of steel (SJR235) in aqueous NaCl (0.5wt.%, pH 8.3 ± 0.5) with carboxyphosphonic acid **4** and NaOH, TEA, Tau (sodium salt), AHX (sodium salt) and Glu (disodium salt) as alkaline additives. A) Development of open circuit potential (OCP) with immersion time; B) potentiodynamic polarization curves after 24 h immersion; C) Bode plots of electrochemical impedance measurements; D) Nyquist plots of electrochemical impedance measurements

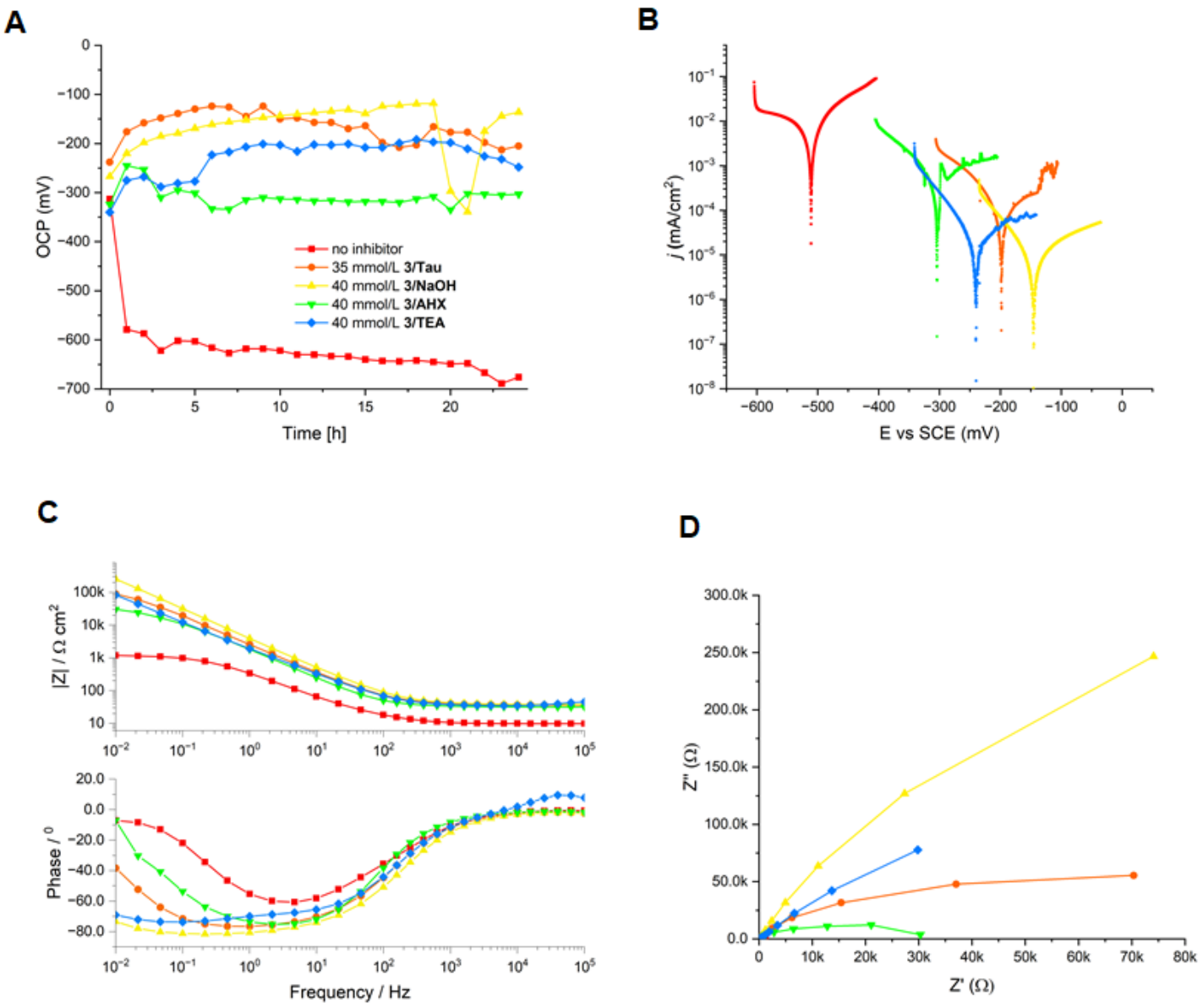

Figure 4

Electrochemical measurements of steel (SJR235) in aqueous NaCl (0.5wt.%, pH 8.3 ± 0.5) with carboxyphosphonic acid **3** and NaOH, TEA, Tau (sodium salt), AHX (sodium salt) and Glu (disodium salt) as alkaline additives. A) Development of open circuit potential (OCP) with immersion time; B) potentiodynamic polarization curves after 24 h immersion; C) Bode plots of electrochemical impedance measurements. D) Nyquist plots of electrochemical impedance measurements

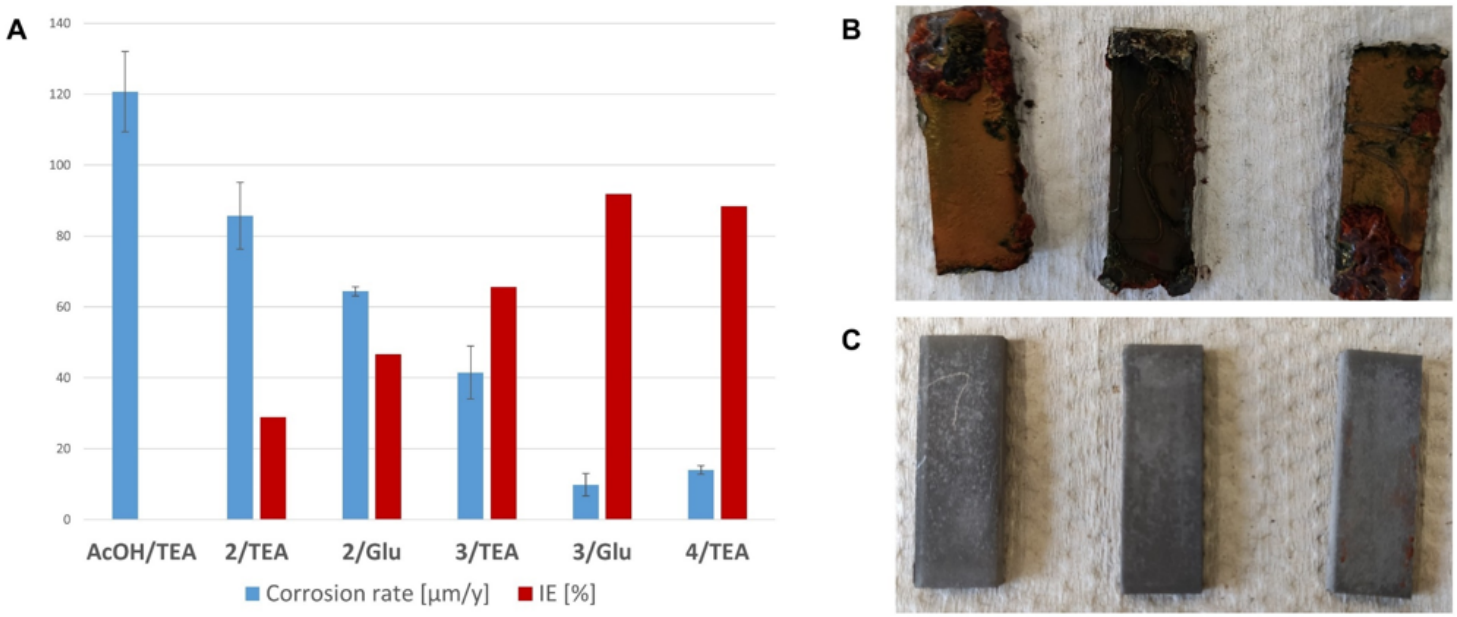

Figure 5

A) Results of the gravimetric tests on S235JR. Rectangular steel slides (30 × 10 × 3 mm) were immersed in test solutions containing 3wt% of the acidic CI for 12 weeks at rt. 1.5 molar equivalents of an alkaline additive for each acidic proton in acidic CIs were added. Medium: aqueous 2wt.% NaCl solution (pH 8.3 ± 0.5). IE was calculated for each CI in relation to the non-inhibited experiment (AcOH/TEA buffer). B) Staining of steel slides after 12 weeks exposure to aqueous **2**/TEA and C) **2**/Glu

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- GraphicalAbstract.png
- NaundorfetalSI.pdf
- Scheme1.png