# The film formation and corrosion inhibition of oleylamines on aluminium

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Film forming amines (FFAs), also called fatty amines or polyamines, are used as corrosion inhibitors in closed cooling/heating systems as well as in steam generators. Due to their volatility they are able to protect the whole water/steam cycle by the formation of a thin film on the metal surfaces, which acts as a barrier between the corrosive agents in the water and the metal.

The use of aluminium alloys in water-steam cycles is getting more and more important in recent years, especially for dry cooling towers. However, aluminium corrosion as well as transport and re-deposition of aluminium are serious concerns and are not well understood. The current technical guidelines for the treatment of water-steam cycles do not consider the aluminium based materials.

Oleylamines, commonly applied FFAs, have been reported as efficient corrosion inhibitors for multi-metal closed cooling systems and water/steam cycles. In order to evaluate their efficiency under the specific conditions of a water-steam cycle containing aluminium, adsorption onto surfaces and corrosion inhibition was investigated as a function of pH, temperature, FFA concentration, aluminium alloy and exposure time.

The adsorption of the FFA was studied by immersion of coupons into FFA containing solutions. The average surface coverage was determined by mass balance of the FFA. Corrosion inhibition was measured by electrochemical impedance spectroscopy. Furthermore, it enables to characterise the property of the film.

All EIS spectra could be fitted with good agreement to the experimental data. The spectra showed significant and systematic changes throughout the exposure time. At 20 °C there is a limited effect of the FFA: Initially the polarisation resistance is increased compared to the blank solution, however, the formation of the protective layer seems to be delayed.

At elevated temperature and especially at high pH (9.2) the FFA clearly improves the protection of aluminium. A layer of higher homogeneity and lower porosity is formed on the surface for the FFA containing solution. According to the test results of this study film forming amines can be applied in water/steam cycles containing aluminium.

## 1. Introduction

Film forming amines (FFAs), also called fatty amines or polyamines, are used as corrosion inhibitors in closed cooling/heating systems [1] as well as in steam generators [2-6]. Due to their volatility, they are able to protect the whole water/steam cycle by the formation of a thin film on the metal surfaces, which acts as a barrier between the corrosive agents in the water and the metal.

In the recent years the use of aluminium in the cooling systems has become more and more important. Units with a jet-spray condenser and a dry-cooled heat exchanger tower with aluminium tubes require strict pH control in order to comply with water and steam quality requirements specified in international standards, e.g. form the IAPWS [7].

The utilization of FFA formulations which exhibit molecular basicity and especially those including alkalizing amines should be carefully evaluated due to the pH restrictions inherent to aluminium and due to the possible localized pH increase at film /metal oxide interface [8] which could increase corrosion of aluminium alloys.

Therefore, the film formation of oleyldiamine (OLDA), a commonly applied FFA, on aluminium surfaces has been studied by mass balance experiments as well as with electrochemical impedance spectroscopy (EIS). The studies have been carried out in dependence of temperature, pH value and exposure time. Additionally, the EIS spectra of solutions without FFA, but pH adjusted, were measured.

## 2. Experimental

The adsorption kinetics of FFA and the average surface coverage of aluminium by FFA were studied by mass balance experiments. Electrochemical impedance spectroscopy was used to characterize the inhibitive properties of FFA containing solutions and to compare their anticorrosion efficiency with untreated medium (blank).

### 2.1 Test solutions

All studies, with the exception of some adsorption studies, were carried out with solutions of 4 mg/L OLDA in de-ionised water (DI-water) with an electrical conductivity below 1.0 µS/cm in order to simulate the conditions in water-steam cycles. The concentration of FFA was chosen to provide enough material to establish a complete film on the test specimen. To ensure the necessary electrical conductivity needed for the EIS measurement 200 mg/L NaCl were added to the test solutions. The pH was adjusted by addition of diluted hydrochloric acid or Sodium hydroxide.

### 2.2 Adsorption studies

The adsorption studies were carried in analogy to the procedure described in [5]: A solution of a defined OLDA concentration in DI-water was filled into a PTFE vessel and degassed with nitrogen to avoid a pH change by carbon dioxide ingress. The solution was stirred by a PTFE coated magnetic stirrer and the solution was heated by a temperature controlled heating unit. Three metal coupons were placed into the vessel, so that they were completely covered by the solution (Figure 1, left). The residual concentration of the FFA in the solution was determined regularly by the bengalrose method described in detail by Stiller at. al. [9] until the concentration in the solution remained constant.

The surface coverage (q) of the coupons with FFA can be calculated from the initial FFA concentration ($c_0$), the FFA concentration in equilibrium ($c_{eq}$), the volume of the solution ($V_S$) and the coupon surface ($A_{Me}$) according to equation 1.

$$q = \frac{V_S}{A_{Me}} \cdot \left(c_0 - c_{eq}\right) \tag{1}$$

Analogous experiments without coupons proved, that there is no significant adsorption of the FFA onto the vessel surface. The FFA concentration is constant within the analytical uncertainty (Figure 1, right). The adsorption experiments were carried out with OLDA for different aluminium alloys at 20 and 60°C.

OLDA does not adsorb onto the aluminium surfaces spontaneously, but the adsorption has come to equilibrium after some days. The adsorption follows with good approximation a first order kinetic: figure 2 shows as example the linear dependence of the plot of $\ln(c_t/c_0)$ versus time for oleyldiamine on steel (left) and aluminium (right). $c_t$ is the concentration measured at the time t. The slope of the regression line is the relative reaction constant of the elimination of the FFA from solution, which is the negative metal adsorption constant k.

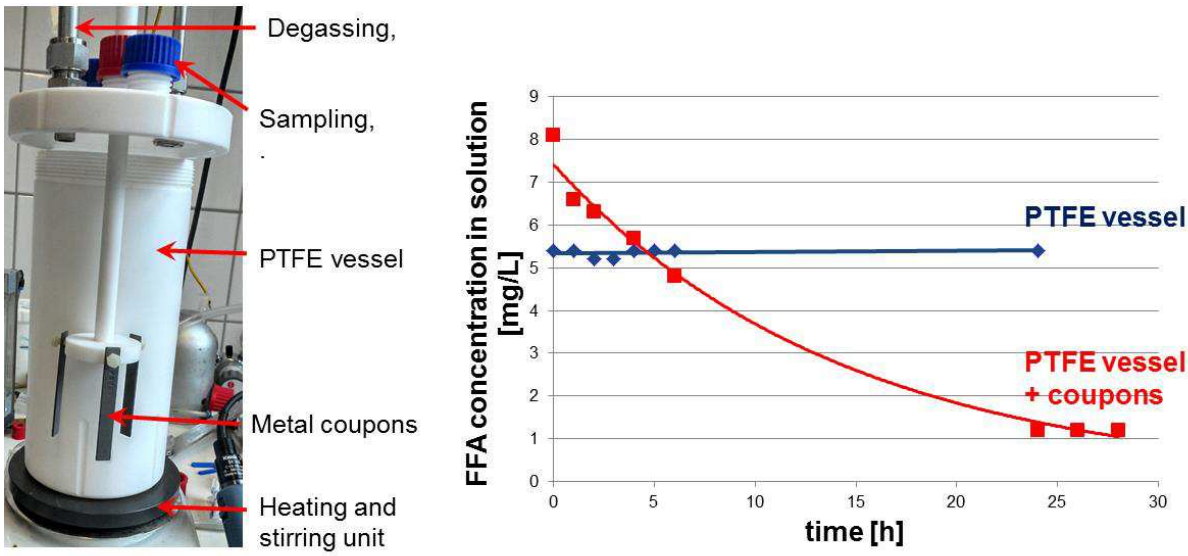


**Figure 1:** (left): Experimental setup for the determination of film forming amine adsorption on metal surfaces.

(right): Example for the dependence of the FFA concentration on time with and without coupon placed in the solution.

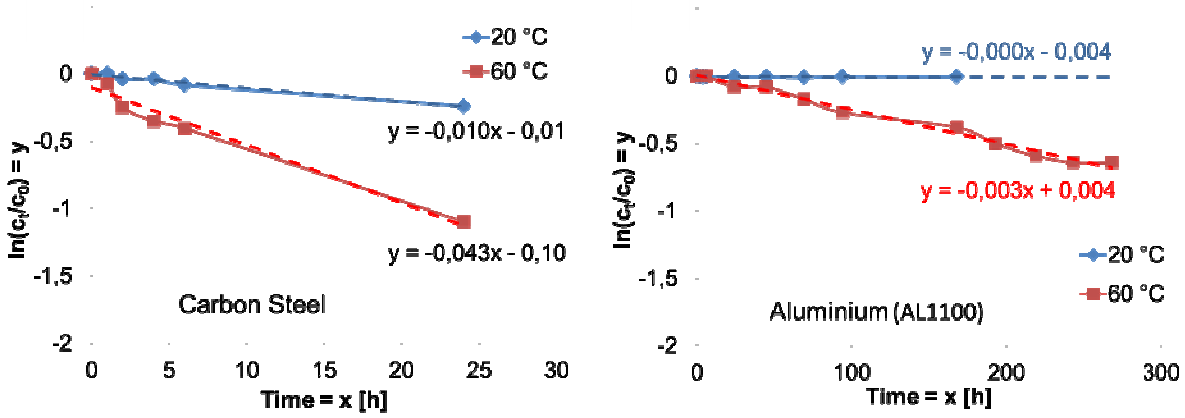


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**Figure 2:** Evaluation of adsorption of oleyldiamine on steel (left) and aluminium (right) by first order kinetic ($\ln(c_t/c_0) = - k \bullet time$)**.**

### 2.3 Corrosion testing

Electrochemistry is a powerful tool to study corrosion phenomena and widely applied in academic and industrial research [10–12]. Therefore, this method was chosen for this study.

Electrochemical measurements were carried out using an Autolab Metrohm frequency response analyser with an electrochemical interface. The impedance diagrams were plotted at the corrosion potential after 2 hours of immersion in a frequency range of 65 kHz to a few mHz with eight points per decade. For the study of the film formation on time a maximum of 11 measurements were carried out within a total period of 48 h.

The corrosive medium was a 200 mg/L NaCl solution in demineralized water in contact with air maintained at the given temperature. The choice of this medium was based upon the following criteria [13]: (i) its low electrical conductivity is close to that encountered in industrial water circuit, (ii) its corrosivity is fairly high, and (iii) it is an easily reproducible baseline solution.

The pH of the OLDA containing test solution without pH adjustment was approx. 8.5. The pH was adjusted to the desired value by adding NaOH (for pH increasing) or HCl (for pH decreasing).

Representing the most important type of aluminium used in the water/steam cycles aluminium 1000 was used as sample material. For all the experiments, the sample materials were polished with SiC paper grade 4000, cleaned in ethanol and demineralized water and then dried in warm air.

For the test samples, the working electrode was a rotating disc consisting of a rod of 1 cm² cross-sectional area to ensure uniform thickness of the diffusion layer at the

electrode surface and a heat-shrinkable sheath leaving only the tip of the cylinder in contact with the solution. All experiments were carried out at a rotation speed of 500 rpm. A silver/silver chloride electrode was used as reference and the counter-electrode was a platinum grid.

The aluminium steel/solution interface was mathematically described in terms of electric equivalent circuits consisting of a resistance electrolyte in series with one or two parallel constant phase element (CPE)/resistor combinations. The semicircular shape of the impedance diagrams allowed the modeling with an equivalent circuit having the following characteristic parameters: Rp, polarization resistance and CPE, double layer capacitance. The CPE which is described by two parameters (capacity $Y_0$ and exponent n) is generally attributed to the roughness and inhomogeneity of the surface or to a non-uniform distribution of the current density on the electrode undergoing corrosion [14, 15].

## 3. Results and discussion

### 3.1 Adsorption experiments

Two different aluminium alloys have been chosen for the adsorption experiments: Al 1100 (AlMg1) and Al 5052. The adsorption for Al 5052 is significantly quicker than Al 1100 both at 20 and 60 °C (Figure 3). At 20 °C no significant reduction of the OLDA concentration in the test solution could be observed for Al 1100, thus adsorption of OLDA practically does not take place. At 60 °C the adsorption is faster and leads to higher surface coverages.

Figure 4 shows a comparison of the adsorption constant and the surface coverage for test specimen from different materials measured at 60 °C. The data for carbon steel, stainless steel and copper have been taken from the literature [16]. All data have been determined with an initial concentration of 5 mg/l OLDA except for Al 1100, where the concentration was 4 mg/l.

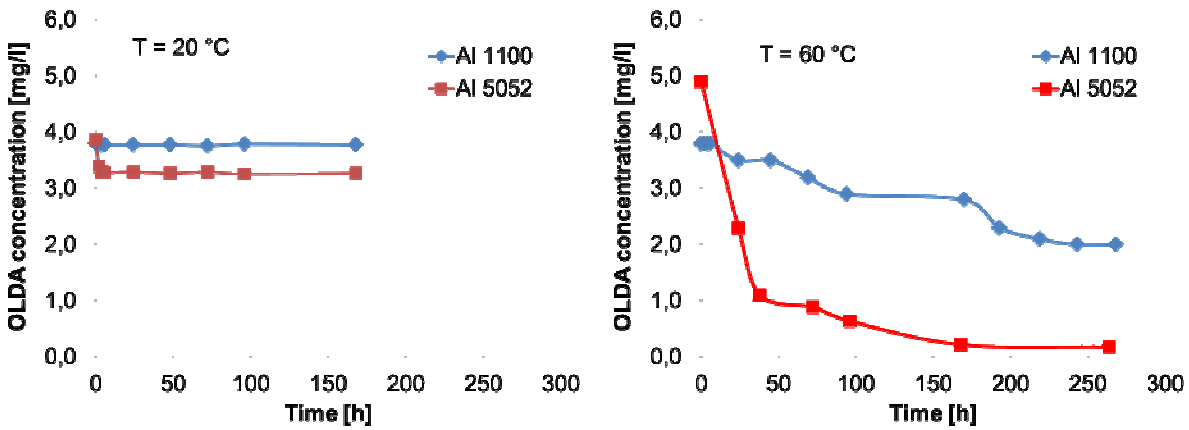


**Figure 3:** Dependence of OLDA concentration on time in test solution with coupons from different aluminium alloys at 20 °C (left) and 60 °C (right).

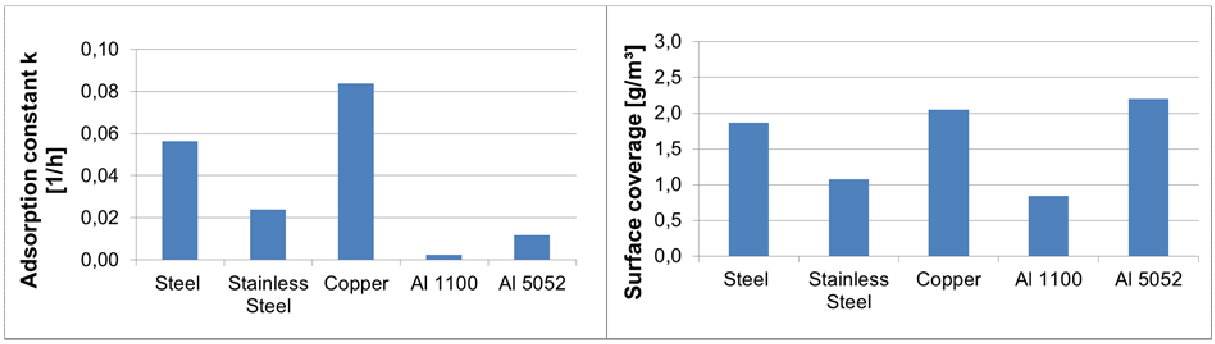


**Figure 4:** Adsorption constant k (left) and surface coverage (right) of OLDA as a function of coupon material. The initial OLDA concentration was 5 mg/l (Al 1100: 4 mg/l) and the temperature 60 °C.

OLDA adsorbs on all five tested metals at 60 °C. Apparently it adsorbs much quicker on copper and carbon steel than on stainless steel and the two aluminium alloys tested. There is more than an order of magnitude difference between the adsorption constants (copper: 0.084/h; Al 1100: 0.002/h). In contrast to this the final surface coverage in equilibrium does not change that much, i.e. it is between 0.84 g/m³ (Al1100) and 2.2 g/m³ (Al 5052). The span in surface coverages will partially be caused the individual surface finishing of the coupons materials, which will result in different roughness and microscopic surface size. Unfortunately, exact data were not available.

### 3.2 Electrochemical impedance spectra

For all test solutions a series of 11 measurements were carried out over a total period of 24 h. The individual spectra were measured after 0, 0.5, 1, 2, 4 8, 16, 24, 36 and 48 h.

The EIS spectra were analysed with 'Fit and Simulation' module of the Autolab® NOVA software, version 1.11.2, from Metrohm Autolab B.V. Generally, the very low (below approx. 0.02 Hz) and the very high frequencies (above approx. 2500 Hz) were not taken into consideration. In some cases the spectra showed significant distortion in the low frequency range, so that more data points were ignored for the fit.

The target was to use for all spectra the same electrical equivalent circuit (EEC) in order to better describe the changes over time. For all spectra one of the EECs from Figure 5 was used for the fit. The EIS spectra measured at 20 °C were fitted with $EEC_1$, because data fitting with $EEC_2$ provide highly instable results for $CPE_2$ and $R_2$. Therefore, both series were analysed taken as a basis $EEC_1$, although the series with FFA could be better described with $EEC_2$. Figure 6 shows two examples of measured and simulated EIS data in the Nyquist representation.

Both electrical equivalent circuits used to analyse EIS data consist of the solution resistance $R_S$, the polarisation resistance Rp in parallel with a capacitance which are the parameters corresponding to the film. The second capacitance associated or not to a charge transfer resistance $R_2$ describes the faradic processes, frequency dependant electrochemical and diffusion phenomena occurring on the electrode surface.

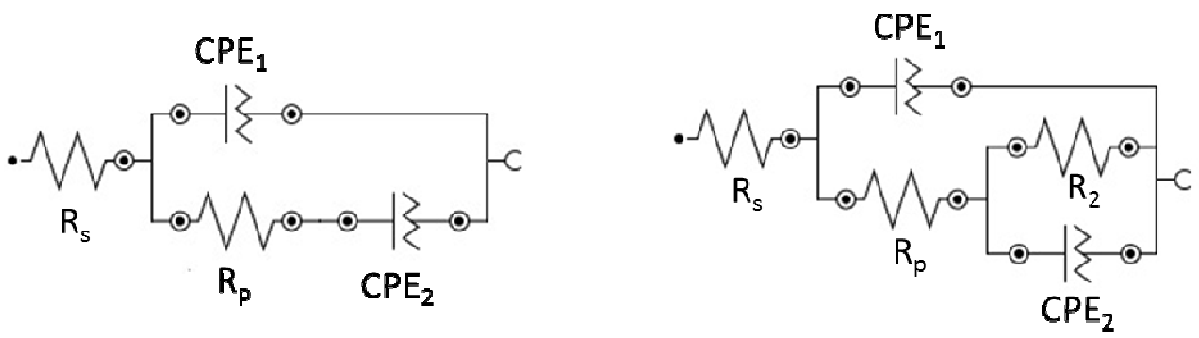


**Figure 5:** Electrical equivalent circuits (EEC) used for the fit and simulation of EIS spectra of aluminium treated with aerated DI-water with and without film forming amine:

(Left) $EEC_1$ used for EIS spectra measured at 20 °C

(right) $EEC_2$ used for EIS spectra measured at 50 °C.

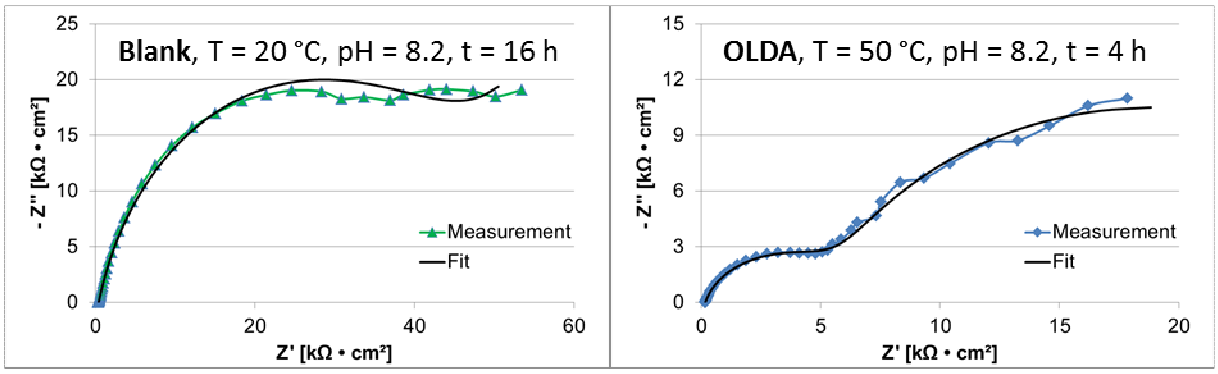


**Figure 6:** Comparison of measured and fitted data of Electrochemical Impendence Spectra

(left): Blank fitted with electrical equivalent circuit 1 ($EEC_1$).

(right): OLDA fitted with electrical equivalent circuit 2 ($EEC_2$).

The impedance of a double layer frequently does not behave as an ideal capacitor. Therefore, the constant phase elements CPE were used in order to fit more accurately the impedance behaviour of the electric double layer and to compensate deviations and non-homogeneity brought by surface roughness in the system.

### 3.2.1 EIS spectra obtained at 20 °C and pH 8.2

Figure 7 shows the EIS spectra obtained at 20 °C and a pH of 8.2 for the blank (top) and the solution containing 4 mg/L of OLDA (bottom). A marked dependence of the spectrum shape on time can be noted for both test solutions. For both solutions the diameter of the high frequency loop is increasing. At the end of the test series the structure of the EIS spectrum is almost vanishing, but the fit results without the second constant phase element ($CPE_2$) were not satisfying.

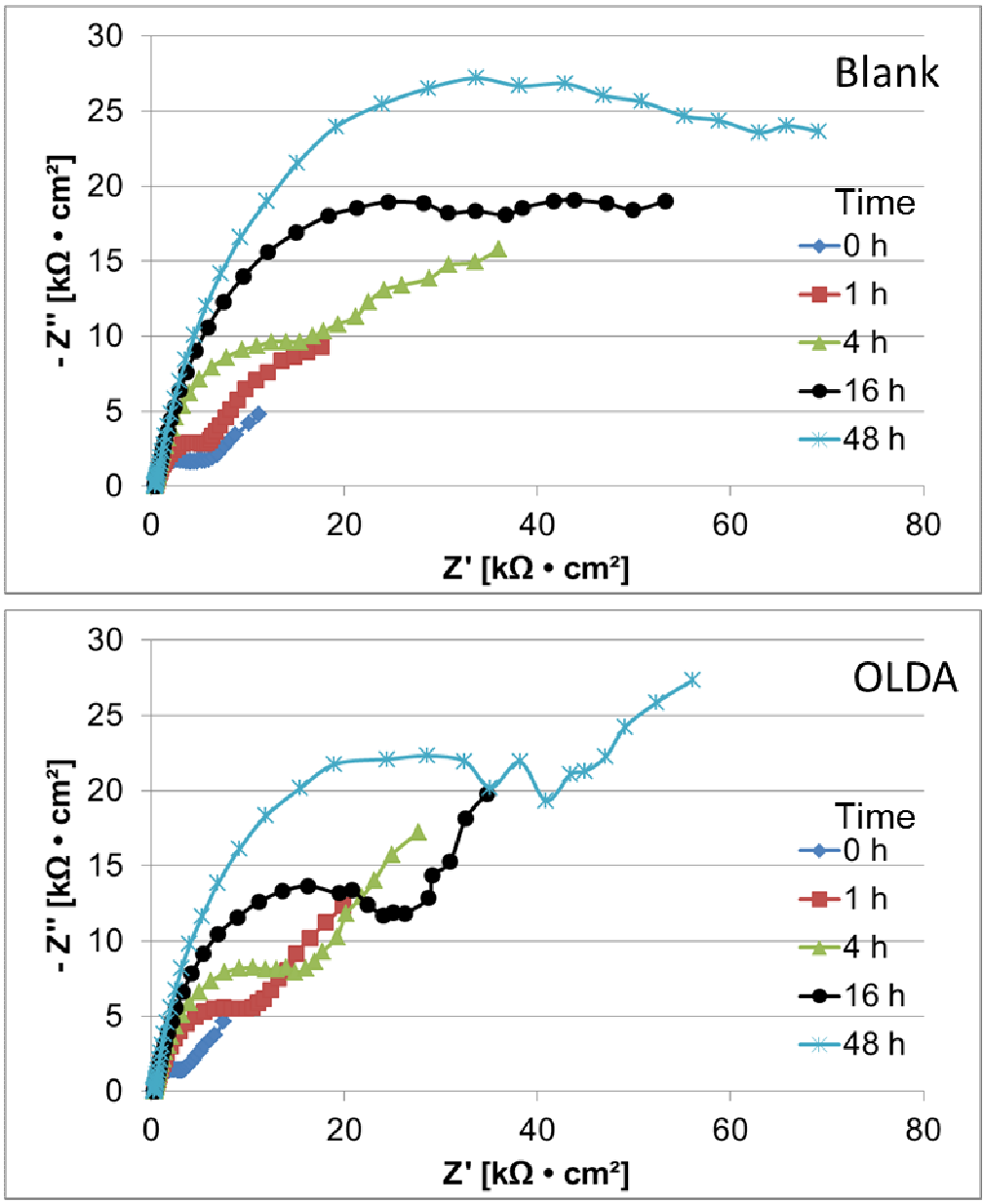


**Figure 7:** Dependence of electrochemical impendence spectra at 20 °C and a pH of 8.2 on time for the solution without inhibitor (Blank) **(top)** and the solution based upon film forming amine (OLDA) **(bottom)**.

It can be noted that the shape of the EIS spectrum in presence of OLDA was characterised by a straight line in the low frequency part of the curve, whatever the immersion time. This behaviour was not observed for the curves of the blank.

As the polarisation resistance value has to be extrapolated to zero frequency, this kind of shape indicates that the anticorrosion protection is very high because of a polarisation resistance value approaching infinity.

Although the shape of some spectra indicates a Warburg type behaviour, i.e. diffusion controlled transport phenomena, only the fit of the spectra of the blank between 1 and 24 h provided a value for the exponent of $CPE_2$ close to the theoretical value of 0.5. A Warburg type impedance is the special case of a constant phase element with the exponent of 0.5.

Figure 8 shows the fit parameter by $EEC_1$ as a function of time. The solution resistances (not shown) were (0.41 ± 0.02) kΩ•cm² for the blank respectively (0.35 ± 0.02) kΩ•cm² for the FFA containing solution.

It can be noted that the polarization resistance after 4 h determined in the blank solution is an order of magnitude higher for aluminium (7.5 kΩ•cm²) than for steel (0.7 kΩ•cm²) measured under the same conditions [18], which is clearly reflecting the higher protecting level of aluminium in this pH range due to the aluminium oxide layer.

The protection, i.e. the polarisation resistance, of aluminium is higher for the first 10 hours in the OLDA containing solution, but thereafter the formation of the protective layer is delayed compared to the blank (Figure 8a). The two curves parallel with the same slope after 24 hours. The protective effect of the film forming amine is much stronger on steel than on aluminium under this condition.

However, the decrease in capacitance of the film simultaneously with the increase of the resistance would reflect the formation of a protective layer on the surface. Indeed the decrease in double-layer capacitance can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer. So it can be related to the adsorption of OLDA on the metal surface.

Several authors [19, 20] have confirmed that the conductance was directly depending on the porosity of the protective layer adsorbed on the surface: the lower the capacitance the lower the porosity.

$$C_{dl} = \frac{\varepsilon_o \varepsilon}{\delta} S \qquad (2)$$

$\delta$ is the thickness of the protective layer, S is the electrode area, $\varepsilon_0$ the vacuum permittivity and $\varepsilon$ is dielectric constant of the medium.

A capacitance reduction may result if water molecules at the electrode interface are largely replaced by organic inhibitor molecules through adsorption. The larger inhibitor molecules reduce the capacitance through the increase of the double layer thickness, and the decrease in the porosity.

Furthermore, the roughness of the layer formed in the OLDA containing solutions finally is lower, i.e. its homogeneity is higher, since the exponent of the constant phase element ($CPE_1$) is above the one from the blank and reached a value of 0.867 after 48 h. It increases constantly for the OLDA solution instead of being constant for the blank (0.827 ± 0.005). Also the exponent of the $CPE_2$ is higher for the OLDA solution, but finally equals (Figure 8f) the value of the blank. The capacities $Y_0$ of both CPEs show no significant differences between the two solutions (Figure 8b, e).

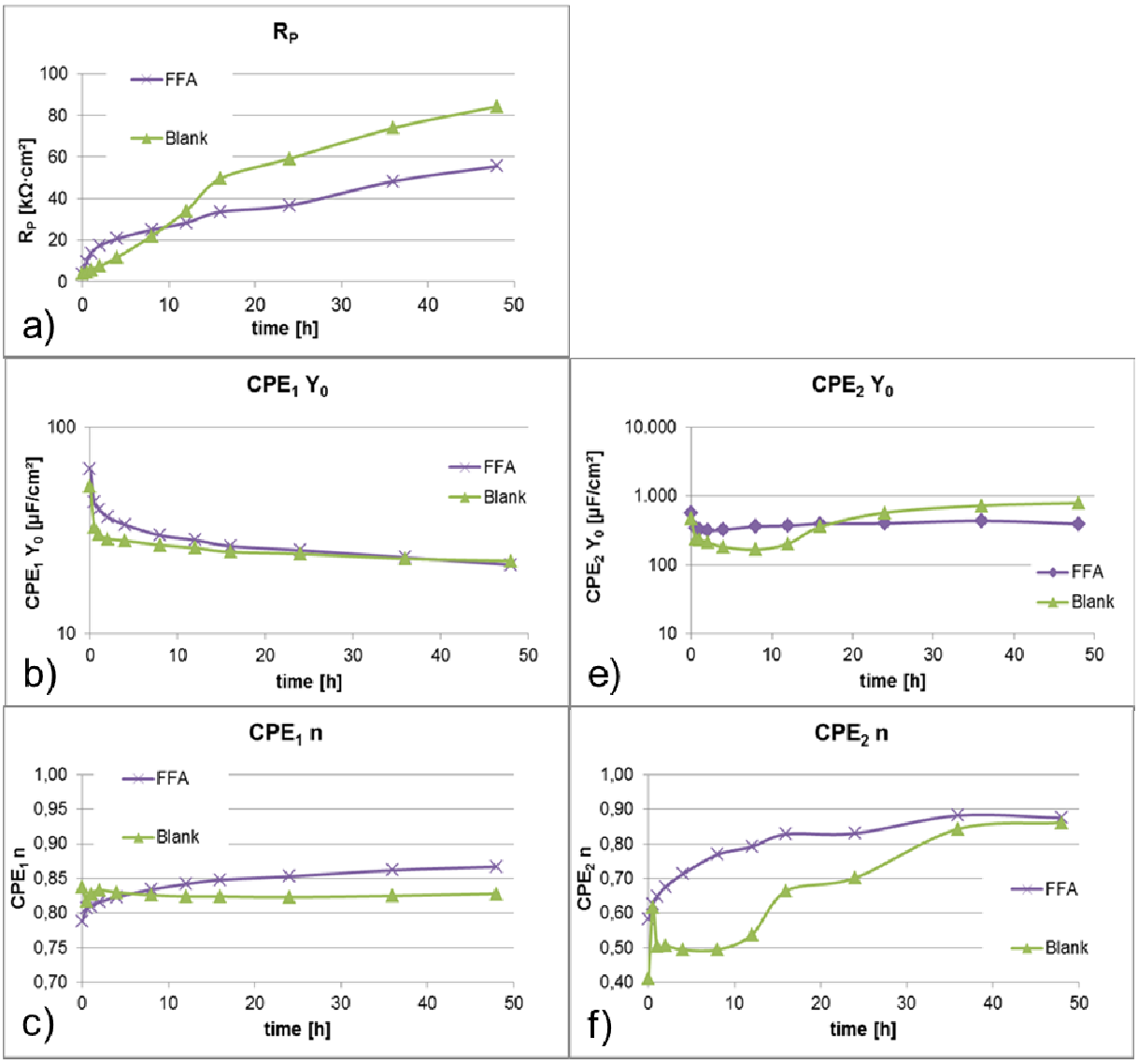


**Figure 8:** Dependence of **a)** polarisation resistance $R_P$ and constant phase element (CPE) parameters - **b), e)** capacity $Y_0$ and **c), f)** exponent n - derived from electrochemical impedance spectra on time for solutions without inhibitor (Blank) and with film forming amine (OLDA). The data fit used the electrical equivalent circuit 1 ($EEC_1$).

Temperature: 20 °C; pH: 8.2

### 3.2.2 EIS spectra obtained at 50 °C and pH 8.2

The temperature of condensates in water-steam cycles may vary locally between 20 °C and up to about 60 °C in the warmer zones of the heat exchanger. Due to the limitations of the measuring cell the water temperature could not be controlled well above 50 °C. Therefore, analogous studies were done at 50 °C.

Figure 9 shows the EIS spectra obtained at 50 °C and a pH of 8.2 for the blank (top) and the solution containing 4 mg/L of OLDA (bottom). Also in this case a marked dependence of the spectrum shape on time can be noted for both test solutions. For both solutions the diameter of the high frequency loop is increasing. Unfortunately, the high frequency part of the EIS spectra after 24 h of the OLDA containing solutions were so distorted, so that an evaluation would have been senseless. Therefore, they have not been taken into further consideration.

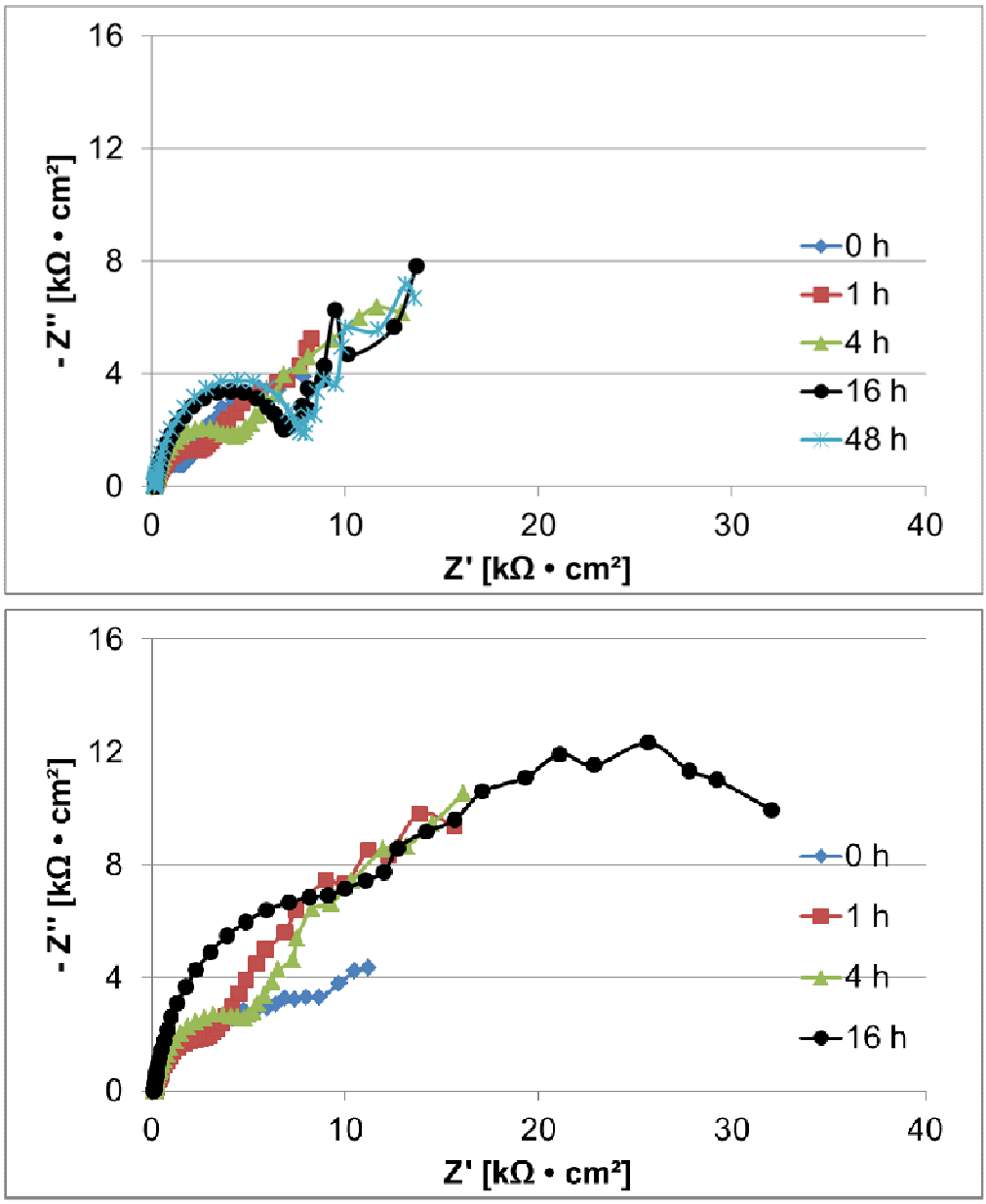


**Figure 9:** Dependence of electrochemical impendence spectra at 50 °C and a pH of 8.2 on time for the solution without inhibitor (Blank) **(top)** and the solution based upon film forming amine (OLDA) **(bottom)**.

Figure 10 shows the fit parameter by $EEC_2$ as a function of time. The solution resistances (not shown) were (0.20 ± 0.03) kΩ•cm² for the blank respectively (0.16 ± 0.04) kΩ•cm² for the FFA containing solution.

At 50 °C the polarization resistance and resistance 2 are higher for the OLDA containing solution than for the blank, with the exception of the 24 h value of $R_2$. (Figure 10a, c). This indicates the formation of a better protective layer in the presence of the film forming amine. However, the level of protection at 50 °C is lower compared to 20 °C. Furthermore, the polarization resistance is still increasing at 20 °C, whereas at 50 °C the value for the blank seemingly has reached a stable value. Whether $R_P$ was still increasing for the OLDA solution cannot be unambiguously judged. The data of both constant phase elements don't show significant differences between the two solutions (Figure 10, b, c, e, f).

### 1.1.1 EIS spectra obtained at 50 °C and pH 9.2

Water-steam cycles treated with all volatile treatment generally are operated at a pH value of at least 9.2 in order to protect the steel surfaces. This high pH levels are not recommended for aluminium containing water-steam circles. In order to study the impact of pH excursions, e.g. caused by lack of control of ammonia dosage, a series of EIS spectra was measured at 50 °C and a pH of 9.2, simulating realistic worst case conditions.

Figure 11 shows the EIS spectra obtained at 50 °C and a pH of 9.2 for the blank (top) and the solution containing 4 mg/L of OLDA (bottom). Again the spectrum shape changed with time for both test solutions. In both cases the diameter of the high frequency loop is increasing over time. It should be noted that the axis-scales for the blank are four times magnified.

Figure 12 shows the fit parameter by $EEC_2$ as a function of time. The solution resistances (not shown) were (0.20 ± 0.01) kΩ•cm² for the blank respectively (0.30 ± 0.02) kΩ•cm² for the FFA containing solution. The spectrum of the blank solution after 48 h could not be measured due to loss of test solution.

The polarisation resistances $R_p$ and $R_2$ both are clearly higher for the OLDA containing solution than for the blank (Figure 12a, c). The comparison of the data obtained at a pH of 8.2 demonstrates that a high pH is detrimental for aluminium, since the polarisation resistances are clearly lower at pH 9.2. $R_p$ after 24 hours is more than double at 8.2 than at 9.2 (8.4 respectively 4.1 kΩ•cm²). The difference is even bigger for $R_2$: it only reaches 2.6 kΩ•cm² at pH 9.2 compared to 17.7 kΩ•cm² for the lower pH. This confirms the increased activity of Al dissolution reaction (transfer charge) at high pH. The effect of pH increase on corrosion of aluminium expectedly is opposite to steel [18].

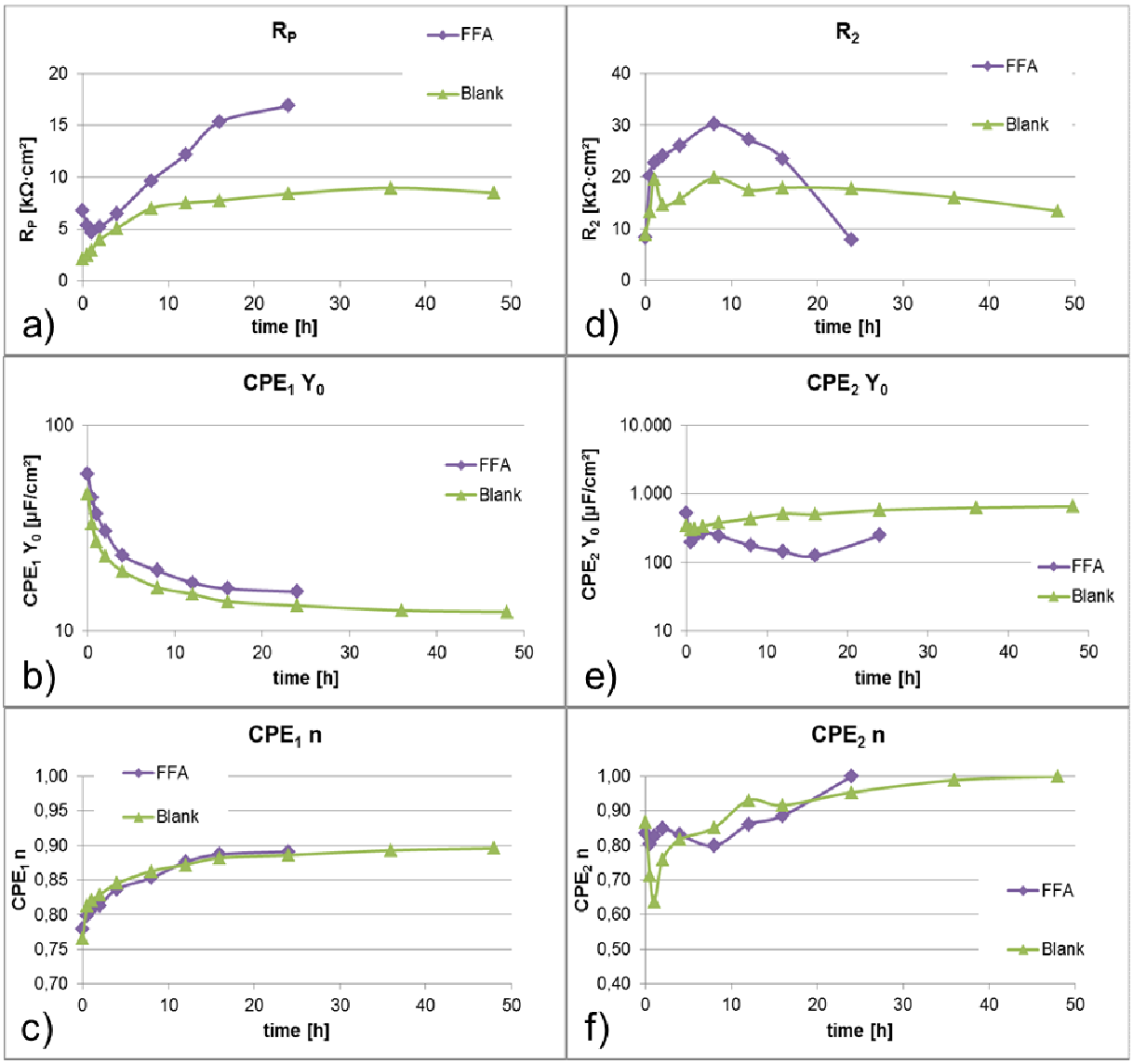


**Figure 10:** Dependence of **a)** polarisation resistance $R_P$, **c)** resistance 2 $R_2$ and constant phase element (CPE) parameters - **b), e)** capacity $Y_0$ and **c), f)** exponent n - derived from electrochemical impedance spectra on time for solutions without inhibitor (Blank) and with film forming amine (OLDA). The data fit used the electrical equivalent circuit 2 ($EEC_2$).

Temperature: 50 °C; pH: 8.2

The effect of the pH increase is much smaller for the film forming amine containing solutions. Indeed, after 24 hours the determined value of $R_P$ at a pH of 9.2 is below the value at 8.2 with film forming amine (9.3 kΩ•cm² versus 15.4 kΩ•cm²), but still above the blank value at 8.2 (8.4 kΩ•cm²). So, with the addition of OLDA the detrimental effect of a pH increase can be successfully compensated. The increase of resistance value in presence of OLDA together with a strong decrease of capacitance at the same time indicates a formation of a protective layer with a low porosity on the metal surface. Table 1 shows a survey of the resistance data.

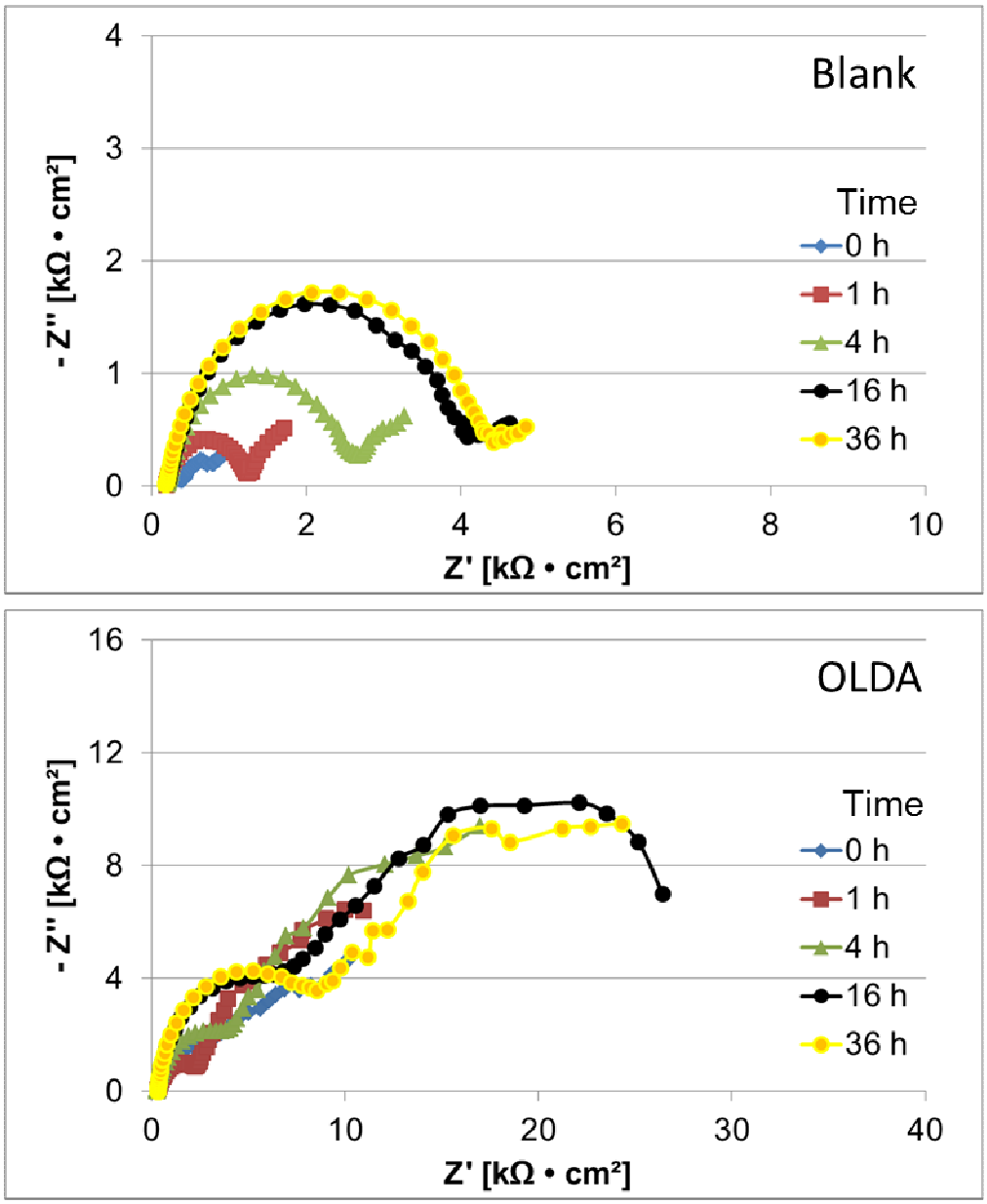


**Figure 11:** Dependence of electrochemical impendence spectra at 50 °C and a pH of 9.2 on time for the solution without inhibitor (Blank) **(top)** and the solution based upon film forming amine (OLDA) **(bottom)**.

Note the different axis scales.

For both constant phase elements the exponents are higher for the OLDA containing solution (Figure 12c, e), indicating the formation of less rough and more homogenous layer on the aluminium surfaces compared to the blank. For $CPE_1$ the exponent is increasing with time and reaches 0.928 after 36 hours, a value close to an ideal capacity, whereas it remains constant for the blank: 0.86 ± 0.01.

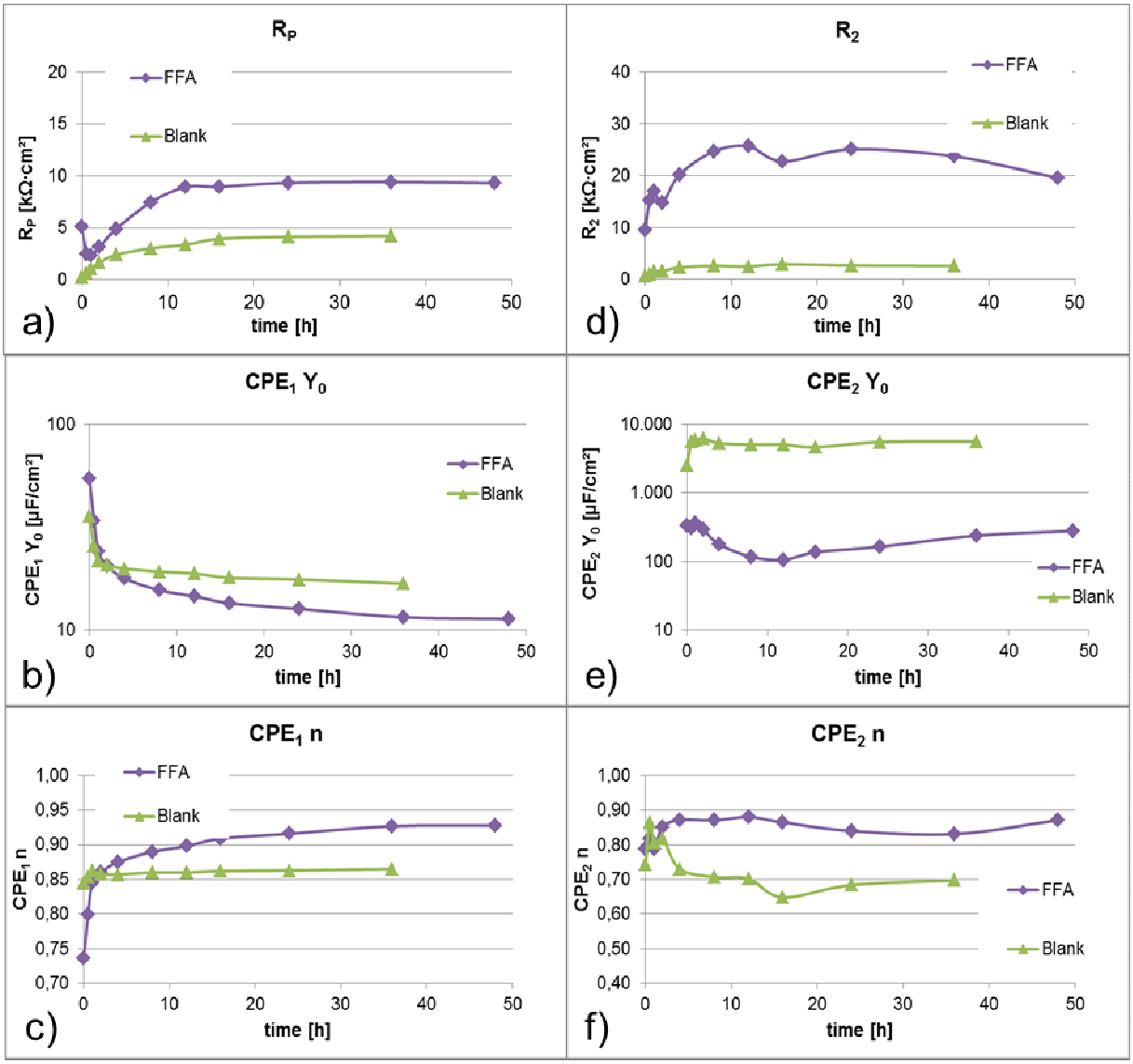


**Figure 12:** Dependence of **a)** polarisation resistance $R_P$, **c)** resistance 2 $R_2$ and constant phase element (CPE) parameters - **b), e)** capacity $Y_0$ and **c), f)** exponent n - derived from electrochemical impedance spectra on time for solutions without inhibitor (Blank) and with film forming amine (OLDA). The data fit used the electrical equivalent circuit 2 ($EEC_2$).

Temperature: 50 °C; pH: 9.2

The lower exponent in combination with the higher capacity in $CPE_2$ shows that for the blank solution a less homogenous and more porous layer is formed, which has significant lower corrosion protection than the OLDA containing solution. Also the resistance is on a much lower level. The EIS spectra clearly demonstrate the inhibitive effect of OLDA at this pH.

**Table 1:** Survey of the resistance data $R_P$ and $R_2$ derived from EIS spectra for test solutions without (Blank) and with film forming amine (OLDA) after 24 hours of exposure.

| | $R_P$ [kΩ•cm²] | | $R_2$ [kΩ•cm²] | |
|---|---|---|---|---|
| | Blank | OLDA | Blank | OLDA |
| pH: 8.2; T: 20°C | 59.2 | 37.7 | | |
| pH: 8.2; T: 50°C | 8.4 | 16.9 | 17.7 | 7.8 |
| pH: 9.2; T: 50°C | 4.9 | 9.3 | 2.6 | 25.1 |

## 2. Conclusions

The adsorption and corrosion behaviour of aluminium alloys has been studied under simulated condensate conditions of water-steam cycles with and without the addition of oleyldiamine (OLDA), a widely used film forming amine for the treatment of steam generators.

The adsorption rate of OLDA on aluminium increases with temperature and is depending on the type of alloy. The rate at 60 °C is significantly lower than of other metals (steel, stainless steel, copper), but the final average surface coverage is in the same order of magnitude. At 20 °C the adsorption rate is very low and could not be quantified.

The main objective of this study was to investigate the impact of OLDA on the corrosion of aluminium. Electrochemical impedance spectroscopy (EIS) was applied at 20 °C and 50 °C for two pH values: 8.2 and 9.2. The resulting spectra show a distinct dependence on time. This indicates that the adsorption is not spontaneous. It did not come into equilibrium for all experiments, especially for the experiment at 20 °C.

The spectra all show a distinct high frequency loop, in some spectra two loops could be observed. All EIS spectra were mathematically described by two different electric equivalent circuits using constant phase elements. The evolution of the parameters was determined over time for up to 48 hours.

At 20 °C OLDA leads to an increased initial corrosion protection, but later to a delayed formation of the protective layer, that was not finished until the end of the experiment. However, with OLDA a less porous layer compared to the blank is formed.

Temperature increase of the test solutions leads to a decrease of corrosion protection reflected in a clear reduction of the polarisation resistances. There is a clear protective effect of OLDA compared to the blank. However, the evaluation was limited to a period of 24 hours. No significant differences in the layer characteristics could be found.

The increase of pH from 8.2 to 9.2 led to a strong decrease of the resistances of the blank. OLDA shows a clear protective effect, which can be seen in the higher resistances measured. The porosity of the layer is lower compared to the blank.

According to this study OLDA has a small effect on the corrosion protection of Aluminium at 20 °C, whereas at elevated temperatures it provides better protection compared to the untreated water for both tested pH values. Therefore, it can be concluded, that it can be applied in water-steam cycles containing aluminium. For a definite conclusion additional questions have to be addressed, such as the influence of OLDA on aluminium transport.

## 3. Acknowledgement

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## 4. References

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