

## Supporting information

# N-*b*-Hydroxyethyl Oleyl Imidazole as Synergist to Enhance the Corrosion Protection Effect of Natural Cocoyl Sarcosine on Steel

Saad E. Kaskah <sup>1,\*</sup>, Gitta Ehrenhaft <sup>2</sup>, Jörg Gollnick <sup>2</sup> and Christian B. Fischer <sup>1,3,\*</sup>

<sup>1</sup> Department of Physics, University Koblenz-Landau, 56070 Koblenz, Germany

<sup>2</sup> Institute of Mechanics and Material Science, TH Mittelhessen University of Applied Sciences, 35390 Giessen, Germany

<sup>3</sup> Materials Science, Energy and Nano-Engineering Department, Mohammed VI Polytechnic University, 43150 Ben Guerir, Morocco

\* Correspondence: saadelias82@googlemail.com (S.E.K.); chrbfischer@uni-koblenz.de (C.B.F.); Tel.: +49-261-287-2345 (C.B.F.)

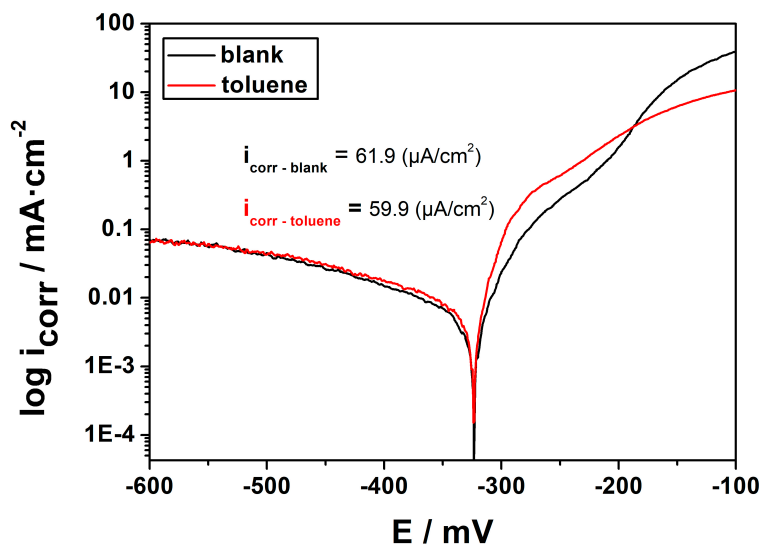
**Abstract:** To investigate the corrosion protection behavior of naturally derived cocoyl sarcosine in combination with N-*b*-hydroxyethyl oleyl imidazole for steel CR4 in 0.1 M NaCl, different evaluation systems (weight loss, electrochemical measurements, and spray corrosion tests) were used. Both compounds were tested in different concentrations (25–100 mmol/L) and with variable dip coating times (1–30 min), first individually and then in combination, to check any synergistic effects for surface protection. Both showed only an insignificant corrosion inhibiting effect with less than 50% efficiency at all concentrations and dip coating times if used alone. In contrast, compound combinations revealed an improved corrosion inhibition correlated with higher concentrations. Across all methods, the compound combination concentration of 100 mmol/L resulted in improved efficiency of up to 83% for gravimetric tests, up to 84% for the impedance measure and more than 91% for potentiodynamic polarization. Dip coating variations proved 10 min to be the best option for all compounds with a maximum efficiency of up to 86% for the compound combination.

**Keywords:** protective film; synergistic effect; low carbon steel; dip time effects; image processing

## **List of contents**

<b>Page S3:</b>	<b>SI 1:</b> PP measurements for steel CR4 with toluene compared to blank in 0.1 M NaCl.
<b>Page S4:</b>	<b>SI 2:</b> PP measurements for steel CR4 with different concentrations of C, OI, and C+OI in 0.1 M NaCl
<b>Page S5:</b>	<b>SI 3:</b> Individual EIS spectra for compounds OI, C and combination C+OI of different concentrations in 0.1 M NaCl
<b>Page S7:</b>	<b>SI 4:</b> PP measurements for steel CR4 in 0.1 M NaCl for different immersion times in 50 mmol/L of C, OI, and C+OI
<b>Page S8:</b>	<b>SI 5:</b> Linear slope values from Figure 7c – plotting the root of relative corrosion area against exposure time

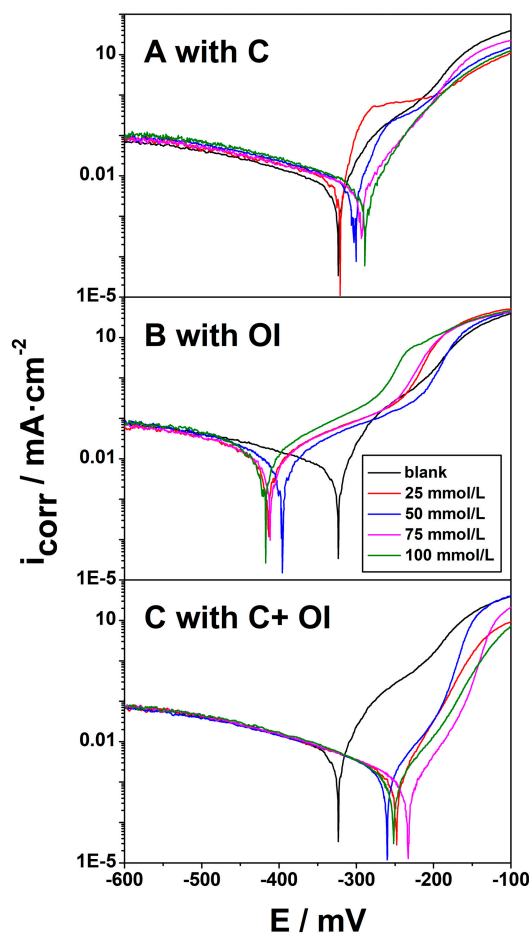
# **SI 1: PP measurements for steel CR4 with toluene compared to blank in 0.1 M NaCl**



**Figure S1:** PPs for steel CR4 immersed in toluene (red) compared to blank (black) in 0.1 M NaCl.

Figure S1 shows the anodic and cathodic polarization for uncoated and steel CR4 immersed for 10 min before in toluene (which is later used as solvent for the compounds C and OI). The as prepared samples were used as working electrode in 0.1 M NaCl. Before a potential of  $\pm 200$  mV (according to OCP value) was applied a 30 min equilibration time to reach a stable OCP was set. No change in potential ( $E_{\text{corr}}$ ) and only a very small decrease for current density ( $i_{\text{corr}}$ ) could be detected, which is concluded as a neglecting effect of toluene on the protection/corrosion process.

## SI 2: PP measurements for steel CR4 with different concentrations of C, OI, and C+OI in 0.1 M NaCl

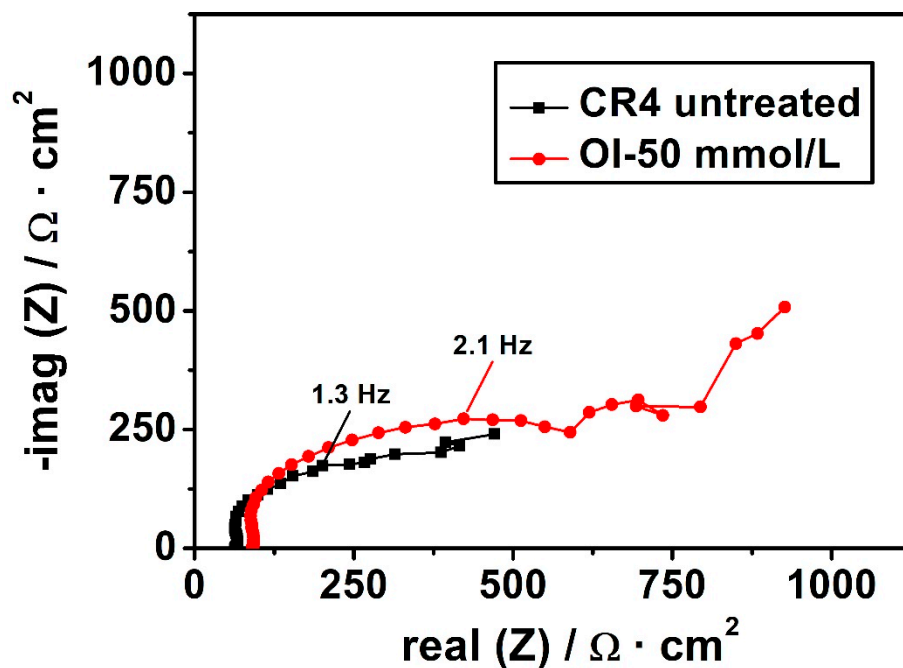


**Figure S2:** PPs with present substances: **A** for only C, **B** for only OI, and **C** for C+OI at different concentrations of 25 (red), 50 (blue), 75 (magenta), and 100 mmol/L (green) in 0.1 M NaCl. Blank material is displayed in black.

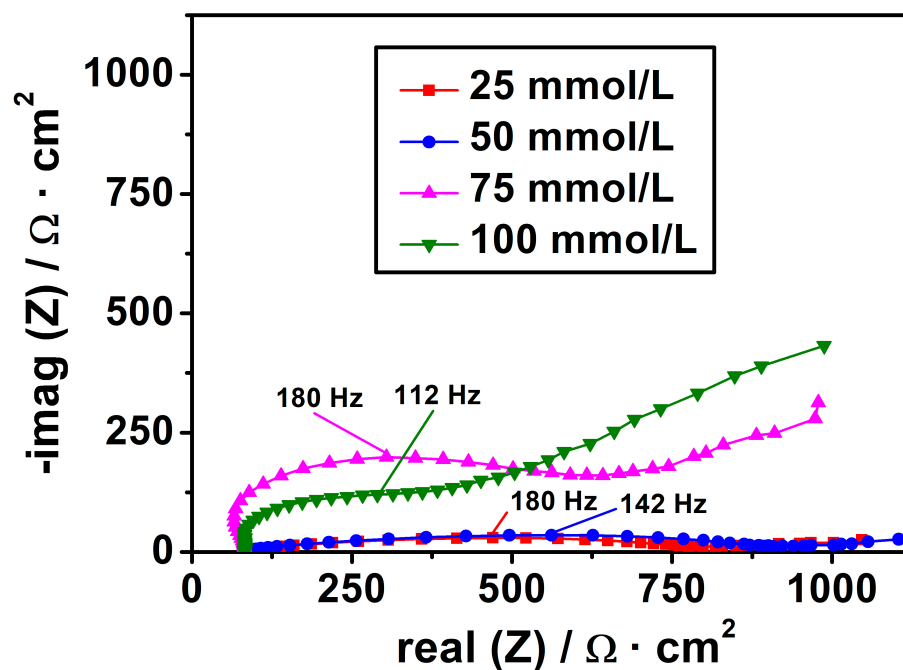
Figure S2 shows the anodic and cathodic polarization course for C, OI, and the combination C+OI at different concentrations (25, 50, 75, and 100 mmol/L, according color code) in 0.1 M NaCl in comparison to the blank steel CR4 (black). Almost no decrease could be detected in the cathodic current for all C concentrations while anodic current decreased except for 25 mmol/L (Figure S2A), with an overall slight shift in corrosion potential in positive direction. Compound OI only slightly decreased the cathodic current but more the anodic course, while a strong shift of the corrosion potential into the negative direction took place (Figure S2B). The best efficiency to reduce the corrosion current density was obtained with the combination C+OI with a simultaneous strong shift of the corrosion potential in the positive direction (Figure S2C).

**SI 3: Individual EIS spectra for compounds OI, C and combination C+OI  
of different concentrations in 0.1 M NaCl**

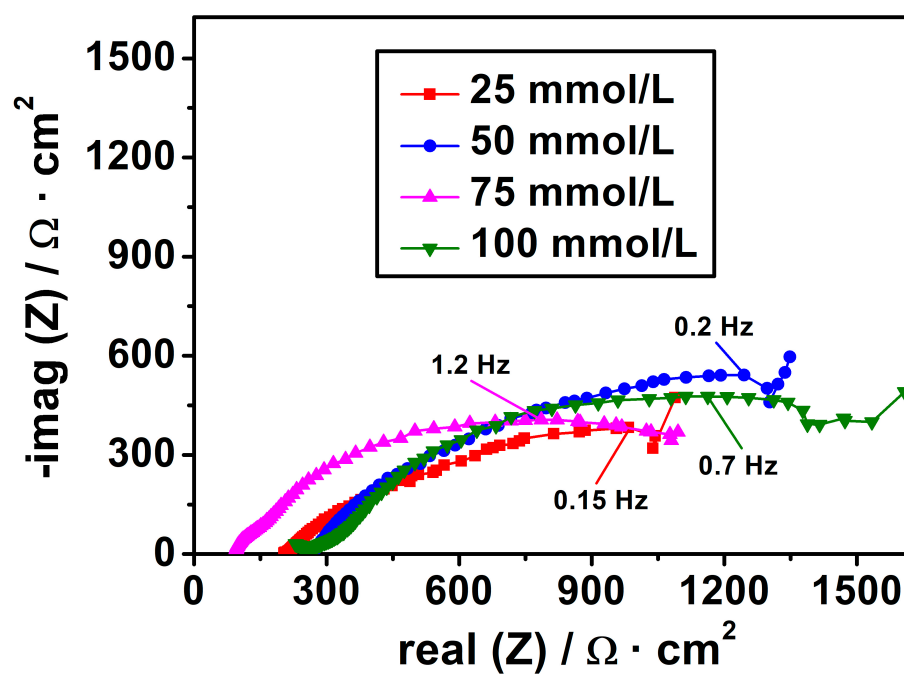
**Extended Figure 4a** for untreated CR4 and 50 mmol/L OI



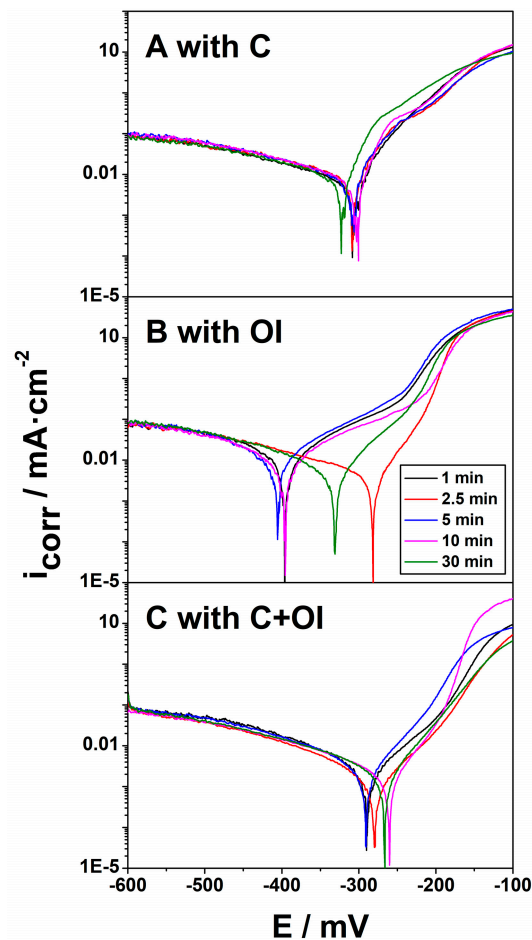
**Extended Figure 4b** for compound C



Extended Figure 4c for compound combination C+OI



**SI 4: PP measurements for steel CR4 in 0.1 M NaCl for different immersion times in 50 mmol/L of C, OI, and C+OI**



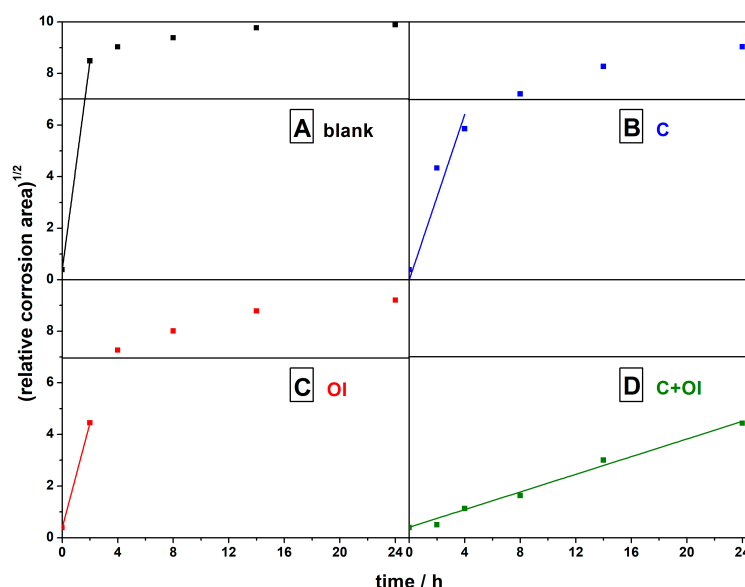
**Figure S3:** PP for steel CR4 at different immersion times (1, 2.5, 5, 10, and 30 min, according color code) in 50 mmol/L of C (A), OI(B), and C+OI(C) each.

Figure S3 shows the PP of different immersion times (1, 2.5, 5, 10, and 30 min, according color code) of steel CR4 in the toluene solution of C (A), synergist OI (B), and C+OI (C). The curves show that the general behavior does not change with immersion time and that the shift in corrosion potential is related to the concentration effect. From the polarization course, it can be seen that increasing the immersion time of the steel sample in the compound solution increases the protective effect, as the adsorption on the metal surface is enhanced or more homogeneous when more molecules are available. The efficiency increased between 1 to 10 min. For durations longer than 10 minutes, the efficiency remains the same or even decreases slightly, which is why 10 minutes seems to be the best time for immersion here.

## SI 5: Linear slope values from Figure 7c – plotting the root of relative corrosion area against exposure time

**Table S1:** Detected relative corrosion areas and relative number of corrosion spots of ten independent samples for each compound series in comparison to the blank material at specific exposure times.

Time [h]	Relative corrosion area [%]				Relative number of corrosion spots [cm <sup>-2</sup> ]			
	blank	with C	with OI	with C+OI	blank	with C	with OI	with C+OI
2	72.03	18.76	19.79	0.25	568.6	759.8	1321.6	1967.9
4	81.54	34.28	52.79	1.27	296.5	741.5	746.3	1877.9
8	87.94	51.90	64.05	2.66	137.5	551.4	552.8	1220.6
14	95.34	68.38	77.10	9.04	36.5	375.7	473.8	836.6
24	97.68	81.56	84.63	19.67	11.2	176.9	321.2	434.5



**Figure S4.** Display of the underlying linear regressions from Figure 7c as individual presentations for each corrosion series. The plots show the results as the root of the relative corrosion area versus the five specific exposure times for blank material (A, black), C (B, blue), OI (C, red), and C+OI (D, green).

To get a clearer picture of the present compound efficiencies in the spray corrosion chamber compared to blank material the root of the relative corrosion area detected was used in relation to progressed time (2, 4, 8, 14, and 24 h). Figure S4 (A, B, C, and D) summarizes the respective results for the linear regressions. The resulting slope steepness specifies the susceptibility to corrosion and ongoing behavior of the corrosion process. The efficiency of an inhibitor is higher if the resulting line is flat (e.g. Figure S4D for C+OI). This corresponds to a low corrosion rate indicated by insignificant values for the corrosion areas [6].



**Procedure and results** [6]: The blank metal samples were previously evaluated to obtain the value for detectable “*corrosion*” areas at time zero, which was determined in average to 0.15 %, resp. 0.39 (root of corrosion area). Scanning artifacts of residual particles can cause the deviation from zero due to the cleaning process or due to coloring effects of the crystalline metal structure. This value was used as fixed offset in all linear fittings here.

Figure S4A shows for blank material in the beginning already a high corrosion rate with steep slopes. The metal surface of the blank material was already 72 % covered with rust products during the first 2 h. After 4 h, nearly 82 % was covered and the grate area increased slowly from here over the next 20 h to reach over 97 % after 24 h. From a certain point, the grate area increases not only by expansion but also by coalescence of areas. This could be an indication of the change in steepness of the slope to a flatter behavior. Therefore, a linear regression of all data points for the blank material was not appropriate resp. possible, and the area of high corrosion area with lower expansive growth was excluded in the fit. The limit was set to seven for the root of corrosion area as indicated by the additional horizontal black line in each diagram. All collected data before this value were used in the linear regressions, except for the blank material, since the first point at 2h was already up to eight (Figure S4A).

The plots of Figure S4 for the present compounds C (B), OI (C), and C+OI (D) follow nicely a linear regression for their available data set and clearly show their order I terms of efficiency. The weakest one to suppress corrosion is OI followed by C. The most effective inhibitor with a flatter slope is the synergistic combination of C+OI.