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Investigation of The Reaction Kinetics of Chromium(III) Ions with Carboxylic Acids In Aqueous Solutions and The Associated Effects on Chromium Deposition

L. Büker,[1,2,*,z] R. Dickbreder,[2] R. Böttcher,[1] S. Sadowski,[2] and A. Bund[1,**]

[1]*Electrochemistry and Electroplating Group, Technische Universität Ilmenau, 98693 Ilmenau, Germany*
[2]*Kiesow Dr Brinkmann GmbH & Co. KG, 32758 Detmold, Germany*

Electroplated chromium is an important industrial coating. Both in the decorative and functional field, research is being carried out to develop trivalent chromium electrolytes. In this work, the interaction between Cr[III] ions and carboxylic acids (malonic acid, malic acid, oxalic acid and glycolic acid) is investigated. The use of carboxylic acids to improve the current efficiency in trivalent chromium plating baths has been known for a long time. But the thermodynamics and kinetics of the associated complexing reactions are not well understood. It is shown that the complexes form at different rates depending on the acid and its concentration and have a varying influence on chromium deposition. For the development of a technical bath, care must be taken to ensure that the molar ratios between chromium and carboxylic acids can be controlled. This is possible with the HPLC method presented here.
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Because of restrictions by the European Union regarding the use of hexavalent chromium, there is the strong need for a suitable replacement. The main applications of chromium in the electro-plating industry are functional and decorative coatings. Functional chromium coatings are typically thick ($\gg 1\ \mu m$, often 100 to 200 μm) and are designed for applications where hardness, wear, fatigue and other functional properties are paramount. In contrast, decorative chromium coatings are thin ($<1\ \mu m$) and are used in applications where color and/or reflectivity are paramount. Recent reports showed that hexavalent chromium (Cr[VI]) can be substituted in certain cases (e.g. decorative coatings) by trivalent chromium (Cr[III]).[1]

In the 1970s Cr[III] electrolytes were introduced as alternatives to hexavalent chromium (chromic acid) electrolytes.[2–4] In the late 1990s, researchers at the National Institute of Standards and Technology (NIST) patented a trivalent chromium plating process for the production of hard chromium coatings based on pulsed currents.[5,6] The obtained chromium layers had to be heat-treated to achieve the desired properties. In 2006 Renz et al. reported the application of pulse plating for trivalent chromium plating processes for functional applications.[7] An interesting result was that the pulse-off times had to be 5 to 7 times longer than the on-times to obtain a microstructure with the desired functional properties.[8] In summary, there is impressive knowledge on trivalent hard chromium plating. But there is still limited understanding on the long-term operation of the corresponding plating baths.

There are significant differences between trivalent and hexavalent electrolytes regarding the resulting properties of the deposits. The microstructure of the respective coatings differs, which results in different visual appearance (reflectivity, color, etc).[9] The chromium layers deposited from a hexavalent electrolyte appear bluish while those deposited from a trivalent electrolyte usually appear more yellowish. Due to the higher concentrations of additives and interactions between the chemicals (e.g. sensitivities to foreign metals) it is also more complicated to deposit a uniform Cr layer from a trivalent bath. To improve the performance of these electrolytes, complexing agents such as formic acid,[10] oxalic acid[11,12] or glycine[13] are used (Fig. 1).

Most trivalent chromium electrolytes contain a chromium salt in the form of Cr$_2$(SO$_4$)$_3$ or CrCl$_3$.[14] In this work the reaction between

chromium potassium sulphate (KCr(SO$_4$)$_2$·12H$_2$O) and various organic acids (oxalic acid, malic acid, glycolic acid and malonic acid) has been investigated. The dicarboxylic acids used in this work can interact with the chromium ions via several positions and thus belong to the class of chelate ligands (Fig. 2).[15,16] Chelate ligands form more stable complexes than monodentate ligands. The role of the carboxylic acids is to improve the deposition process. One hypothesis is that the corresponding complexes are easier to reduce than the aquo complex [Cr(H$_2$O)$_6$]$^{3+}$.[14,17–19] As a result the current efficiency should be significantly increased.[20] The electrochemical reduction of Cr(III) proceeds via two consecutive reactions,[14,18,21] Eqs. 1 and 2.

$$Cr^{3+} + e^- \rightarrow Cr^{2+} (E^0 = -0.407\ \text{V}) \tag{1}$$

$$Cr^{2+} + e^- \rightarrow Cr^0 (E^0 = -0.913\ \text{V}) \tag{2}$$
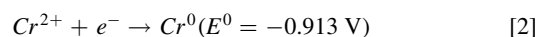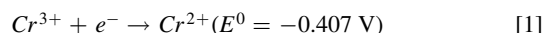
The standard potentials for Eqs. 1 and 2 are both negative. In addition the sluggish kinetics of charge transfer to the aquo complexes lead to high overvoltages.[22] Therefore, the formation of hydrogen is the dominating reaction at the cathode, Eq. 3.

$$2H_3O^+ + 2e^- \rightarrow H_2 \uparrow + 2H_2O \tag{3}$$
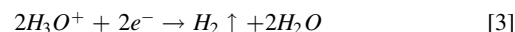
In consequence, the current efficiency of chromium deposition is typically below 20%.[7]

The rate of complex formation between Cr[III] ions and carboxylic acids has not been correlated with chromium plating in detail and the influence of the bath age has often been neglected.

Although the deposition process is improved in terms of current efficiency and visual appearance of the layers, it has also been observed that in some cases the complexing agents reduce the life time of the plating bath. After some time (weeks to months, depending on the electrical charge passed and bath volume) the deposition process is inhibited, which usually is explained with the formation of more stable complexes. The impact of this process on the deposition rate depends on the concentration of complexing agents and is determined by the sluggish reaction kinetics between chromium and the organic compounds. However, it is not yet clear how exactly the mechanism of complex formation proceeds, which complexes are formed and how fast the complex formation takes place.

In this work a method was developed to estimate the formation rates of the complexes between chromium and some carboxylic acids. The combination of this data with results from chromium
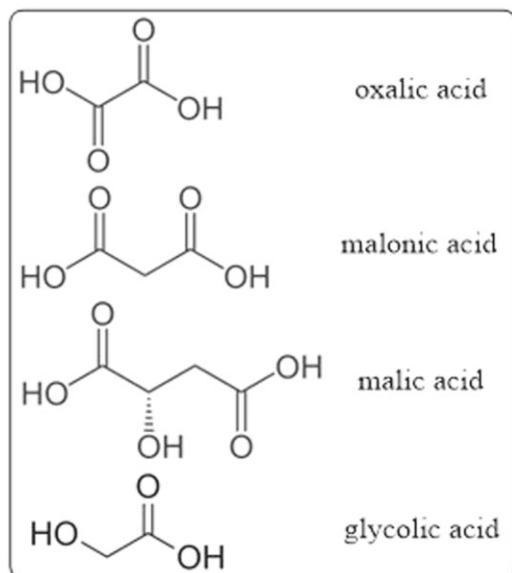
Figure 1. Chemical structures of different carboxylic acids investigated in this work.
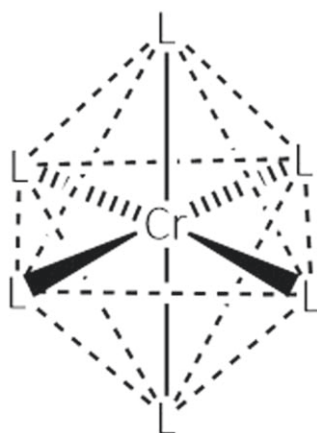

Figure 2. Schematic representation of the different positions of the ligands (L, carboxylic acids) can react with chromium ions.

depositions from these electrolytes leads to a better understanding of the deposition process and its limitations.

Experimental

Chromium deposition as a function of the carboxylic acid used.—To investigate the influence of the carboxylic acids on the chromium deposition, a base electrolyte, containing $0.25\,mol\,l^{-1}$ $KCr(SO_4)_2 \cdot 12H_2O$ was prepared. To this electrolyte $0.125\,mol\,l^{-1}$, $0.25\,mol\,l^{-1}$ or $0.5\,mol\,l^{-1}$ of the respective acid was added and heated up to 60 °C for 3 h to ensure a complete reaction between Cr^{III} and the complexing agent. Subsequently, a buffer $(1.62\,mol\,l^{-1})$ and supporting salt $(1.46\,mol\,l^{-1})$ were added (Table I). Brass sheets $(0.7\,dm^2)$ were pre–treated with Ekasit 028 and Ekasit E53 and coated with a thin nickel underlayer (Orion 4000, KIESOW Dr. Brinkmann GmbH & Co. KG). Afterwards, they were coated in the Cr^{III} electrolytes at $5\,A\,dm^{-2}$ for 7 min which should result in a typical Cr layer thickness of $0.3\,\mu m$. The exact layer thickness was determined by X–Ray fluorescence spectroscopy (XRF, Fischerscope X-ray XDAL 237, Helmut Fischer GmbH).

A usual technical requirement is a slightly bluish color of chromium plated surfaces. The color of coatings can be described with the L*a*b* values. Generally, L* corresponds to light reflectance/absorbance, a* corresponds to red/green balance, and b* corresponds to yellow/blue balance. Specifically, the maximum value for L* is 100 and corresponds to a perfect reflecting diffuser. The minimum value for L* is 0, which corresponds to black. The a* and b* values have no specific numerical limits.[23,24]

Accordingly, the chromium layers deposited in this work are intended to have a high positive L* value and a negative b* value, because they should be replacements for a bright chromium layer from a hexavalent electrolyte. To investigate the influence of the carboxylic acids on the color of the coating, the coated sheets were measured at the same spot and the color was quantified using the L*a*b* values (Spectrophotometer CM-700d, Konica Minolta Business Solutions Deutschland GmbH).

Determination of the reaction rate constants.—In principle ion chromatography (IC) could be used for the determination of carboxylic acids or chromium cations. However, the measuring conditions might change the composition of the electrolyte. To ensure that the free acid and the complexes are separated from each other without decomposition, high pressure liquid chromatography (HPLC) was applied. Thus it is possible to determine the concentration of the acid and the complex in parallel. The stock solutions for the HPLC analytes were prepared as listed in Table II. The separation of the components occurs due to different interaction with the stationary phase. The carboxylic acid component in the solution interacts more strongly with the stationary phase of the HPLC column and is therefore transported more slowly towards the detector. The inorganic component (chromium/complex) hardly interacts with the stationary phase and is flushed more quickly through the column. The components of the baths are thus separated, and their individual concentrations can be evaluated from the area of the detector signal (UV-detector). The operating conditions and essential components of the HPLC device are given in Table III. The mobile phase was diluted perchloric acid and an isocratic method was chosen. The molecules of the samples were detected at 210 nm.

For each series, the stock solutions were freshly prepared. The composition and operating conditions of the solutions are shown in Table IV. Each of the series of measurements comprised fourteen samples: On the one hand solutions with chromium and carboxylic acids with different ratios and on the other hand the pure chromium and acid solutions in corresponding ratios.

A certain portion of each sample was heated to 60 °C for 3 h in order to reach the thermodynamic equilibrium.[19] The pH value was adjusted to 2 (measured using a Portamess, Knick Elektronische Messgeräte GmbH & Co. KG), using H_2SO_4 and NaOH. To characterize the samples via HPLC (Prominence, Shimadzu Deutschland GmbH) they were diluted with deionised water (Ultra Clear UV-Plus, SG Wasseraufbereitung und Regenerierstation GmbH) by a factor of ten.

Results and discussion

Chromium deposition.—In the case of chromium electrodeposition one usually distinguishes between functional (hardness, wear, lubricity, fatigue and the like) chromium and bright chromium (decorative chromium) coatings. The baths investigated here are intended to meet the demands of bright chromium electrolytes with a layer thickness between 0.2 and $0.5\,\mu m$ and a uniform bright layer should be deposited.[25,26]

In order to determine the effect of the concentration of the different carboxylic acids on the deposition, the layer thickness was measured using XRF (Fig. 3). For all acids except malic acid, the layer thickness decreases with increasing carboxylic acid concentration. In the case of malic acid, the layer thickness increases and decreases again with increasing concentration. However, the layer thickness for malic acid containing electrolytes is rather small. Deposition from electrolytes containing glycolic acid and malonic acid (molar ratio of Cr to acid of 1:2 and 1:1) led to layer thicknesses that meet the target values of 0.2–$0.5\,\mu m$. Among the investigated

Table I. Composition of the electrolytes.

Compound	Molar concentration mol^{-1} l^{-1}
KCr(SO$_4$)$_2$·12H$_2$O	0.250
Buffer	1.620
Conducting salt	1.460
Carboxylic acid	0.125
	0.250
	0.500

Table II. Compositions of the stock solutions.

Component	Provider	Purity	Concentration
KCr(SO$_4$)$_2$ · 12H$_2$O	Vopelius Chemie	—	96 g l^{-1} (0.2 mol l^{-1})
C$_3$H$_4$O$_4$	Alfa Aesar	99%	10 g l^{-1} (0.1 mol l^{-1})
C$_2$H$_2$O$_4$ · 2H$_2$O	Acros organics	Extra pure, 99%	10 g l^{-1} (0.1 mol l^{-1})
C$_2$H$_4$O$_3$	Merck	99%	10 g l^{-1} (0.1 mol l^{-1})
C$_4$H$_6$O$_5$	AppliChem	pure	10 g l^{-1} (0.1 mol l^{-1})

Table III. Operating conditions and used HPLC devices.

Device	Description
Pump	LC-20AD, Shimadzu
Auto sampler	SIL-20A, Shimadzu
Column–heater	CTO-20AC, Shimadzu
Column	EC 250/4 Nucleodur C18 Pyramid, 5 μm, Macharey Nagel
Precolumn	Multo High 100 RP, 18–5 μm, Chromatographie-Service
UV–detector	CDD-10A$_{V_P}$
Flow	0.5 ml min^{-1}
Mobile phase	Acetonitril, Pan Reac AppliChem, for UHPLC, 99.9%

Table IV. Compositions of the sample solutions. The chromium stock solution had a concentration of 10 g l^{-1}, and the stock solutions of the carboxylic acids had a concentration of 50 g l^{-1}. The pH value was 2.0.

	Cr	Oxalic acid	Malic acid	Glycolic acid	Malonic acid
ml/50 ml	5	2.5	2.5	2.5	2.5
		5	5	5	5
		10	10	10	10
mol l^{-1}	0,019	0.006	0.005	0.007	0.004
		0.011	0.010	0.013	0.007
		0.022	0.019	0.026	0.015

of Cr layers with adjustable color. In addition, it has been shown that the complexes have a negative influence on the deposition rate. Hence, the use of weaker complexing agents, such as glycolic or malonic acid, would be advantageous. Oxalic acid seems to suppress the deposition significantly with increasing concentration, which is probably due to the stronger complex formation. Malic acid however seems to hardly react with chromium, resulting in hardly any effect on deposition rate at any concentration, contrary to the other acids.

The above discussed results lead to the question about the reason for the different influence of the concentration of the acids on the deposition from the respective electrolyte and the influence of bath age on the complexation and hence the deposits quality. It appears

electrolytes, the depositions from the ones containing oxalic acid illustrate best the negative impact of a too high concentration of the complexing agents. The deposition rate of chromium decreases with increasing concentration of the complexing agents, mostly independent of the pH value, indicating that the formed complexes are too stable and hence the deposition rate strongly decreases if the concentration of carboxylic acids is too high. Hexavalent and trivalent chromium deposits typically differ in their color (Table V). While the L* values are in comparable range, the b* value of trivalent chromium deposits are significantly more positive than the one of the hexavalent coating. The coatings thus appear darker and more yellowish than the deposits from a trivalent electrolyte without carboxylic acids (Fig. 4). Considering these results, it is necessary to further optimise the electrolyte composition so that decorative layers can be deposited from these electrolytes. However, these electrolytes could be a good base for the deposition

that positive or negative influences of the carboxylic acids on the chromium deposition become more apparent over time. For this reason, we investigated the progress of the reaction between chromium and carboxylic acid.

Determination of rate constants via HPLC.—The first HPLC experiments aimed on the optimization of the separation method for different chromium complexes, which turned out to be impossible for the chosen column set–up (Table III). The resulting signals could not be attributed to specific compounds. On the basis of their charge, only theoretical assumptions about separation of the complexes can be made. A comparison with standard solutions for the identification of the peaks was not possible, since such standards do not exist. Therefore, the concentration changes of carboxylic acids in the solutions over time in the presence of chromium have been monitored. From these data the rate of the complex formation can
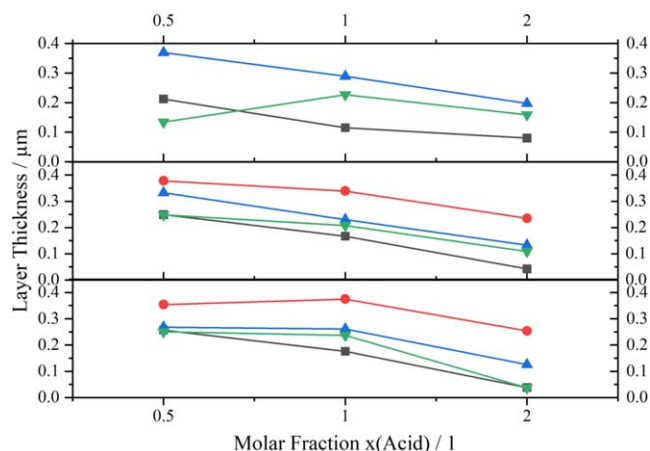
Figure 3. Layer thickness of chromium deposits vs molar fraction of different carboxylic acids and chromium ions for different pH values of 2.1 ± 0,1 (above), 2.6 ± 0,10 (middle) and 3.0 ± 0,10 (below).

Table V. The L*a*b* values of a hexavalent chromium (Saphir 14) and a trivalent chromium coating (Saphir 2000), as provided by Kiesow Dr Brinkmann GmbH & Co. KG, Germany.

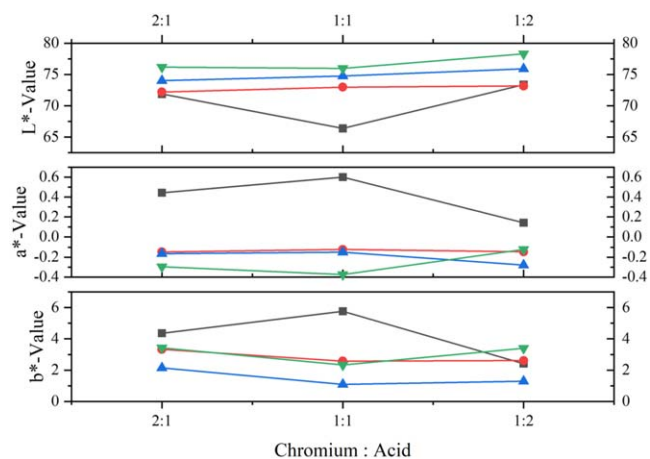|	Saphir 14 (Cr^{VI})	Saphir 2000 (Cr^{III})
L*	80.3	82.0
a*	−0.9	−0.6
b*	−0.6	0.4

Figure 4. L*a*b* values for chromium layers deposited from trivalent chromium electrolytes with different concentration of carboxylic acids (black, oxalic acid; red, glycolic acid; blue, malonic acid; green, malic acid) at a pH value of 2.5.

be estimated. To separate the chromium and acid compounds, the gradient shown in Table VI was used first. When using a gradient, the composition of the mobile phase can be changed while the

Table VI. Used gradient (HPLC), which was initially used to separate the components.

Mobile phase	Time min^{-1}
100% Water (perchloric acid)	0–6
10% Acetonitrile/90% Water (perchloric acid)	6–12
80% Acetonitril/20% Water (perchloric acid)	18
100% Water (perchloric acid)	28

measurement is running. For example, it is possible to achieve a better separation or to accelerate a HPLC method. Subsequently, the method was optimized and only acidified water was used in order to remove algae and fungi. Acetonitrile was used to clean the stationary phase. During the first ten minutes of the measurement all carboxylic acids can be detected (Table VII). Using the HPLC method mentioned above, the reaction rate between chromium and carboxylic acid can be inferred. The reaction rate is proportional to the concentrations of two reactants A and B.[25]

$$v = k[A][B] \tag{4}$$

In Eq. 4 v is the reaction rate in units of mol m^{-3} s^{-1} and k is the temperature dependent rate constant of the reaction in units of s^{-1}.[25] One way to determine the rate law for a reaction is the isolation method, in which all reactants except one are added in excess. Therefore, their concentration can be regarded as constant, because their concentration changes negligibly during the reaction. The concentration of chromium ions $[B]$ was chosen to be significantly higher than that of the carboxylic acids. Replacing $[B]$ with the initial concentration $[B]_0$ yields Eq. 5.[25]

$$v = k[A][B]_0 \text{ with } [B]_0 = const. \tag{5}$$

This rate law corresponds to a first-order reaction. In order to determine the full rate law, this method must be applied to all reactants. For this reason, the acid concentration was increased significantly above that of chromium in another experiment. In Eq. 6 the initial concentration of the carboxylic acids is then given by $[A]_0$.

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \int_0^t -kdt. \tag{6}$$

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt \text{ or } [A] = [A]_0 e^{-kt}. \tag{7}$$

The limits of integration for Eq. 7 are obtained by determining the concentration $[A]_0$ at t = 0[25] and was determined from the solutions without addition of chromium in terms of the peak area measured via HPLC. The peak area for the acid hardly changed during the measuring time (Table VIII). The value for the peak area obtained from the averaged data was proportional to the initial concentration $[A]_0$. The values for $[A]_0$ are shown in Table IX.

The concentration c results from the weighted quantity of the carboxylic acid. P corresponds to the peak area of the acid mixed with chromium, which can be taken from the measured data.

$$[A] = \frac{c(Start)}{[A]_0} \cdot P \tag{8}$$

The determination of the reaction rates is discussed in detail for malonic acid. The values for t and $[A]_0$ were taken from the measured data to calculate the concentration $[A]$ and $[A]/[A]_0$ (Table X). If Eq. 7 applies for the investigated systems, the plot of ln $([A]/[A]_0)$ vs t should be linear. From the slope the rate constant k of the reaction can be determined. In Figs. 5 and 6 the experimental data of the malonic acid reaction with chromium without and with heating are shown. Table XI shows the rate constants k obtained for all carboxylic acids investigated in this work. For the measurements at room temperature all data sets could be evaluated according to the above scheme, but there were no evaluable data for the heated solutions of glycolic acid and oxalic acid, because the measuring points hardly differed from each other. Since the concentration of the acid decreases more strongly compared to the starting concentration, it seems that the reaction becomes much faster by heating up and the reaction can no longer be observed. Thus, no rate constants could be determined for these solutions. Most probably, the complexing reaction advanced too quickly to monitor its progress.

Table VII. Retention time of the carboxylic acids determined with HPLC.

Acid	Retention time min^{-1}
Oxalic acid	4.975 ± 0.002
Malonic acid	7.557 ± 0.004
Malic acid	6.711 ± 0.002
Glycolic acid	5.364 ± 0.002

One important result from the kinetic measurements is that the complex formation follows a pseudo first-order reaction for the reaction of chromium with carboxylic acid at room temperature and the rate constant for the complex formation decreases with increasing ligand size (Fig. 7). The reaction between glycolic acid, which is a monocarboxylic acid that carries an alcohol function instead of a second acid function, and chromium seems to be the slowest. Malic acid reacts slightly faster, but also much slower than malonic or oxalic acid. This behaviour can be explained with the longer chain length of the carboxylic acid. The complex is less

Table VIII. Retention times and peak areas for HPLC measurements for the malonic acid.

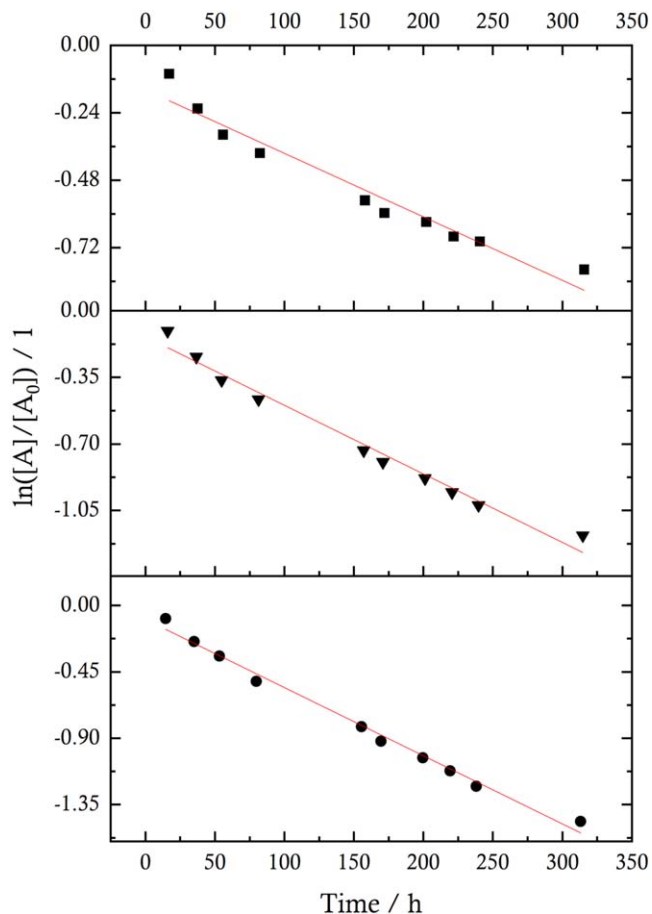| Retention Time min^{-1}	Peak Area/a.u.	Retention Time min^{-1}	Peak Area/a.u.
7.562	99212	7.564	100738
7.558	104348	7.559	106261
7.562	98985	7.564	107204
7.564	106060	7.566	107248
7.556	99997	7.558	101935
7.551	102869	7.551	102840
7.586	95760	7.556	98338
7.577	102246	7.561	101646
7.564	99730	7.561	100170
7.559	102383	7.553	100086

Table IX. Values for the peak area *P* representing the initial concentrations $[A]_0$ for all carboxylic acids.

Acid	Ratio Cr salt: acid	25 °C Peak Area/a.u.	60 °C Peak Area/a.u.
Malonic acid	1:4	101159	102647
	1:2	197627	200686
	1:1	402376	405418
Malic acid	1:4	89123	88417
	1:2	181065	181840
	1:1	373195	373187
Glycolic acid	1:4	66349	66766
	1:3	137338	137186
	1:1	279482	281246
Oxalic acid	1:3	1246646	1256647
	1:2	2527044	2537792
	1:1	5093101	5089572

Table X. The values for the peak area *P*, [A], [A]/[A]$_0$ and *t* determined for the solution of the malonic acid series ([A]$_0$ = 101.159).

Peak Area/a.u.	[A]	[A]/[A]$_0$	Time h^{-1}
101159	2.50 •10^{-2}	1.000	0.0
95637	2.36 •10^{-2}	0.945	15.5
95118	2.35 •10^{-2}	0.940	23.1
85112	2.10 •10^{-2}	0.841	48.0
84154	2.08 •10^{-2}	0.832	75.7
78702	1.95 •10^{-2}	0.778	98.5
62053	1.53 •10^{-2}	0.613	168.1
55758	1.38 •10^{-2}	0.551	207.5
54691	1.35 •10^{-2}	0.541	222.4
50288	1.24 •10^{-2}	0.497	244.8
46040	1.14 •10^{-2}	0.455	260.8

Figure 5. Plot of ln([A]/[A]$_0$) vs time for malonic acid during reaction with chromium at room temperature. Molar ratio of malonic acid:chromium: ■ 1:4, ▼ 1:2 and ● 1:1.

stable, since a large seven-membered ring forms between chromium and the acid, which is energetically more unfavourable than five- or
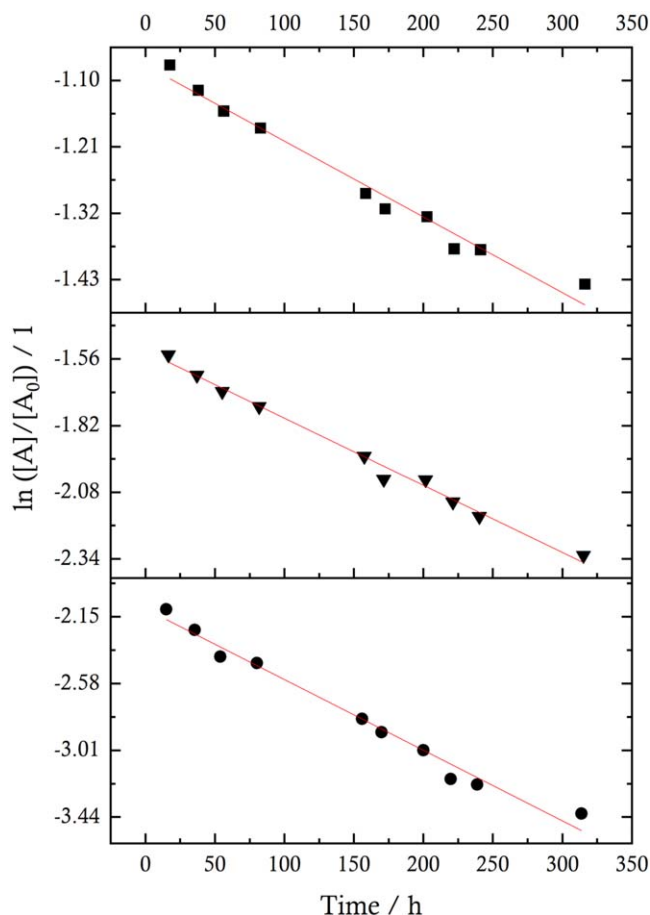
Figure 6. Plot of $\ln([A]/[A]_0)$ vs time for malonic acid during reaction with chromium after the solutions were heated for 3 h at 60 °C. Molar ratio of malonic acid:chromium: ■ 1:4, ▼ 1:2 and ● 1:1.

Table XI. Rate constants k of the complex formation between chromium ions and different carboxylic acids at 25 °C and at 60 °C.

Acid	Rate constant $k/10^3\ s^{-1}$	
	25 °C	60 °C
Malonic acid	-2.3 ± 0.2	-1.3 ± 0.1
	-3.6 ± 0.2	-2.6 ± 0.1
	-4.6 ± 0.2	-4.5 ± 0.2
Oxalic acid	-3.1 ± 0.1	—
	-4.5 ± 0.2	—
	-5.8 ± 0.2	—
Malic acid	-1.10 ± 0.08	-0.36 ± 0.05
	-1.44 ± 0.09	-0.75 ± 0.07
	-1.67 ± 0.06	-0.11 ± 0.10
Glycolic acid	-0.28 ± 0.04	—
	-0.37 ± 0.03	—
	-0.39 ± 0.05	—

six-membered rings that are obtained in the case of malonic- and oxalic acid. The stability of a chelate complex depends on the size of the ligand. The ring stress might be too high and the complex becomes unstable when using multidentate ligands. However, the chelating effect decreases if the chelate ligand forms a ring with a central atom that is too large, causing the interactions and attractive forces to decrease.[27] Ligands optimally form a five- or six-membered ring with the central atom (Fig. 8). The kinetics of the complex formation between chromium and oxalic acid seems to be

faster by a factor of three, compared to the complex formation between chromium and malic acid. The reaction with malonic acid is about three times faster than that of malic acid. Generally, the dicarboxylic acids react much faster, up to a factor of six, than the glycolic acid. All measurements show that the kinetics slow down with increasing acid concentration, which is due to a slower ligand exchange and the steric requirement.

To prove that the decrease in concentration of the free carboxylic acids is due to complex formation with Cr^{III}, the solutions were treated with significantly stronger complexing agents like ethylene-diaminetetraacetic acid and nitrilotriacetic acid (EDTA, NTA). In case of malonic acid, no free acid could be detected after a few weeks, indicating that it was completely bound to the chromium ions. When NTA was added, the malonic acid in the complex was replaced by NTA and could be detected via HPLC. As the retention times of NTA and the other acids are very similar, we refrained from the corresponding experiments.

Furthermore, the reaction of the acids with the chromium ions was visible from distinct color changes of the solutions. The blue Cr^{III} solution turned purple after the addition of the carboxylic acids (Fig. 9). The absorption of the electromagnetic radiation and thus the color depend on the size of the ligand field splitting in the molecules, which is influenced among other factors by the type of ligand and metal ion.[28,29] The color change indicates an increase in the ligand field splitting, since orange light is absorbed without addition of the acid, while yellow and green light is absorbed after their addition. Consequently, the energy required to excite electrons seems to increase. The fact that the peak areas of the pure acid solutions do not change over time proves that the acids are not decomposed. It is also an indication of the reaction between chromium ions and the carboxylic acids, because the peak area of the respective acid becomes smaller in solutions in which acid and chromium are present.

Conclusions

The investigated carboxylic acids have a strong influence on the electrodeposition of chromium. The layer thicknesses are strongly influenced by the concentration and the type of the carboxylic acid. Glycolic acid and malonic acid improve the coating thickness and by interference the current efficiency for chromium deposition. Oxalic acid has the strongest influence on the deposition process. The complex formation is most obvious, as the deposition is strongly inhibited at higher concentrations. It also seems that the carboxylic acids alone are not suitable for a bright trivalent chromium process as they produce dark layers compared to electrolytes without carboxylic acids. To understand the kinetic relationships between chromium and the carboxylic acids, a HPLC method for the determination of the rate constants between dicarboxylic acids and chromium has been developed. The complex formation between Cr^{III} ions and carboxylic acid follows a reaction of pseudo first-order. It was shown that the concentration and size of the ligands reduces the rate constants significantly: the larger the dicarboxylic acid the slower the reaction between the components. The oxalic acid reacts more than six times faster than the glycolic acid. The carboxylic acids which react slower can still have a stronger impact on the electrodeposition process, because the resulting complexes with chromium are weaker.

These results also show the carboxylic acids react relative slowly with Cr^{III} ions. Therefore, initial positive effects can diminish while negative effects might increase with increasing bath age. During the development of a bath, care must be taken to ensure that the molar ratios between the components are controlled carefully. This is possible with the HPLC method presented here, which can support the development and can be used for bath monitoring at the same time.
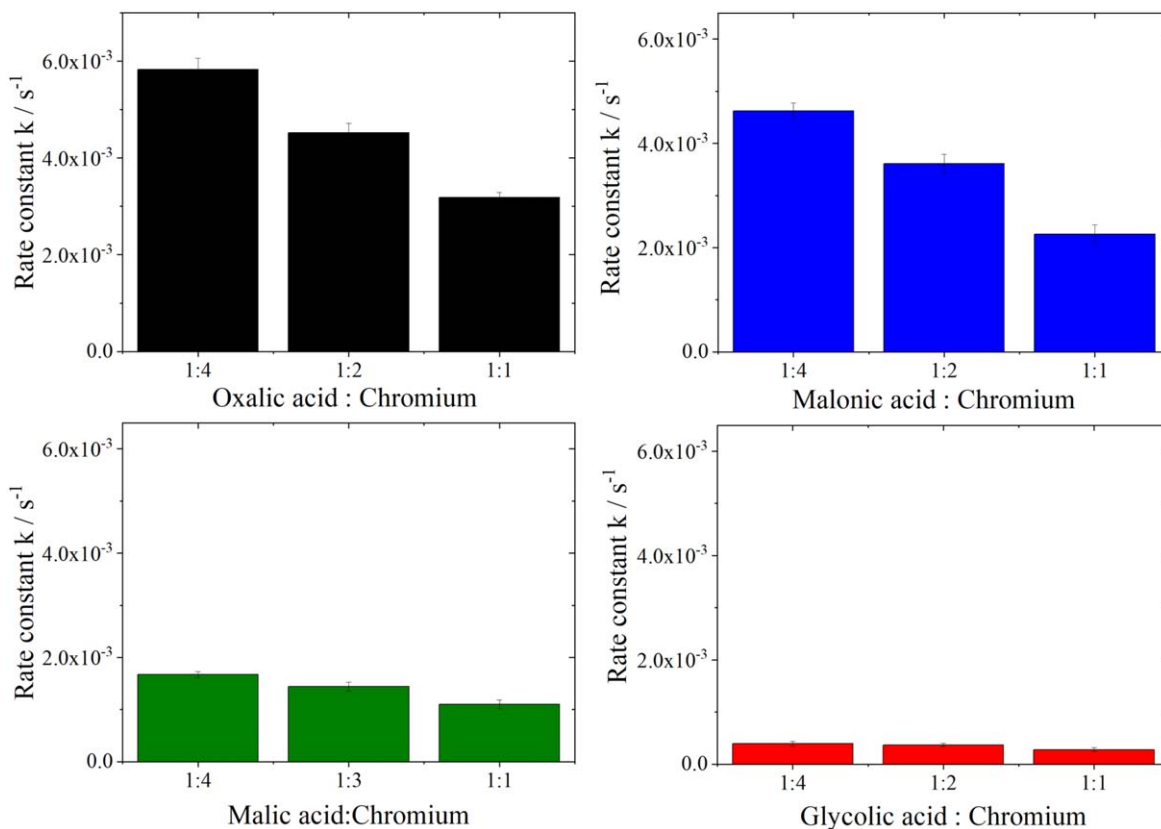
Figure 7. Rate constants for the complex formation between chromium and different carboxylic acids in dependence on their molar fraction at room temperature.
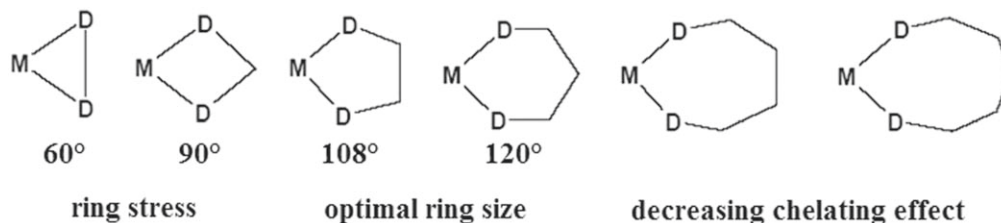

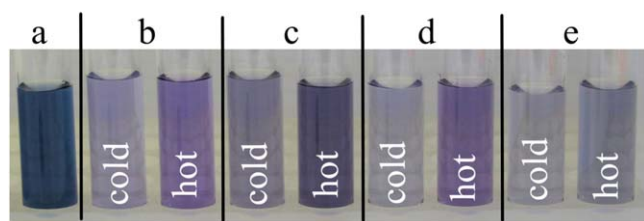**Figure 8.** Influence of the ligand size on the chelate effect.

Figure 9. Color change of the solutions containing (a) only chromium and containing chromium and (b) malonic acid, (c) oxalic acid, (d) malic acid or (e) glycolic acid.

ORCID

L. Büker https://orcid.org/0000-0002-3347-1648

R. Böttcher https://orcid.org/0000-0001-9016-4129
A. Bund https://orcid.org/0000-0001-9837-2408

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