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Kinetics of electrochemical Eu^{3+} to Eu^{2+} reduction in aqueous media

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Abstract

All lanthanides have a stable trivalent oxidation state, but some of them can also occur in the divalent or tetravalent state. Europium is well-known for its divalent oxidation state, which has been investigated in aqueous, organic, and molten salt media. In contrast to other lanthanides, Eu^{3+} can be easily reduced (E^o=-0.34 V vs. SHE) via chemical, electrochemical or photochemical routes, and Eu^{2+} is quite stable in a variety of electrolytes, including nitrate salts. To date, the kinetics of the Eu^{3+}/Eu^{2+} reduction reaction has been investigated only by polarography and chronopotentiometry, most often in perchlorate medium. In this study, the kinetics of the Eu^{3+}/Eu^{2+} couple were analysed in nitrate, chloride and perchlorate media by cyclic voltammetry and linear sweep voltammetry with a rotating disk electrode (RDE). The diffusion coefficient, charge transfer coefficient and rate constants were calculated based on the Levich and Koutecký-Levich analysis and Tafel plot to gain insight in the electrochemical process and the influence of the electrolyte type on it. Given the pre-existing characterization of this redox couple in perchlorate medium, it is selected as a reference system to both compare the kinetic parameters and to validate whether the methodology can be applied to other electrolytes. The Eu^{3+} reduction reaction was found to be quasi-reversible in these electrolytes and the calculated kinetic parameters are in line with the previously reported values.

Keywords: aqueous electrolytes; divalent europium; lanthanides; rare earths; rotating disk electrode

1. Introduction

Lanthanide chemistry is dominated by the trivalent oxidation state and by the gradual filling of the 4f shell across the lanthanide series. However, some lanthanides display unusual oxidation states in the series such as cerium(IV), praseodymium(IV), terbium(IV), samarium(II), europium(II) and ytterbium(II). The divalent europium ion is well characterized, thanks to the facts that the reduction potential of the Eu^{3+}/Eu^{2+} couple is readily accessible ($E°(Eu^{3+}/Eu^{2+})$= −0.34 V), and that the divalent oxidation state is relatively stable due to a half-filled 4f subshell. The electrochemical behavior of lanthanide elements has been extensively studied as model systems in various electrolyte conditions, such as molten salts, ionic liquids, and aqueous/non-aqueous solutions [1–14].

The reduction of Eu^{3+} has been investigated using chemical, photochemical and electrochemical approaches [11,14–21]. The kinetics of the electrochemical reduction reaction have also been investigated using several methods such as polarography, chronoamperometry or voltammetry [22–31]. In earlier works, the kinetics of Eu^{3+} reduction were investigated in aqueous formamide and perchlorate media using a dropping mercury electrode to understand the electrochemical behavior of the system and the influence of viscosity and temperature [29–33]. In these media, the kinetic parameters transfer coefficient (α) and rate constant (k) of the reaction as well as the diffusion coefficient (D) have been calculated. The influence of the formamide concentration on the reversibility was discussed as well as that of the viscosity and pH. In these media, inner-sphere complexation is not very pronounced and Eu^{3+} ions are present mainly in hydrated form. However, with increasing concentration of the electrolyte, a negative shift of the peak potential occurs, which can be explained by the decrease of the solvent activity and lowering the hydration of the europium ions in solution, increasing the entropy. This results in a higher stability of Eu^{2+} complexes

78 [21,31]. Furthermore, the reduction of Eu^{3+} has also been investigated in chloride and nitrate
79 media, with the aim to develop efficient separation processes by change of oxidation state of
80 europium [16,18–20,34–37]. Van de Voorde *et al.* reported that at high aqueous nitrate
81 concentrations, Eu^{3+} can efficiently be electrochemically reduced to Eu^{2+} and that the Eu^{2+} ion
82 is very stable in this system [21]. The Eu^{3+} reduction kinetics and mechanism were also
83 investigated in hydrochloric acid solutions by Atanasyants *et al.* and these authors concluded
84 that the process occurs in the mixed kinetics region [28]. In both studies of Van de Voorde *et*
85 *al.* and Atanasyants *et al.*, a graphite electrode was used instead of a mercury one, and the
86 reactions were found to be quasi-reversible to irreversible based on the electrolyte and the
87 concentrations [21,28]. The effect of non-aqueous solvents such as propylene carbonate and
88 ethylene glycol on the reduction kinetics of Eu^{3+} were also investigated. The kinetic
89 parameters were obtained via chronopotentiometry using a mercury electrode. The Eu^{2+}
90 complexes were found to be stable, but water impurities decreased the stability [10,38]. The
91 aim to gain further insight in the electron transfer reaction of Eu^{3+} reduction led to the use of
92 room-temperature ionic liquids [39] and mixed solvents [40]. Based on this knowledge new
93 electrode materials such as bismuth single-crystal or boron-doped-diamond thin film
94 electrode were tested for the Eu^{3+}/Eu^{2+} redox couple to gain fundamental insight in the
95 electron-transfer kinetics on solid-state electrodes [22,24].

96 Present work is a fundamental study on the reduction kinetics of europium(III) with a
97 conventional solid-state electrode, by cyclic voltammetry and linear sweep voltammetry with
98 a rotating disk electrode (RDE). This work is the first study using a controlled convection
99 method for europium reduction kinetics. Multiple electrolytes such as perchlorate, chloride
100 and nitrate were tested and the results were compared with the existing literature data for
101 perchlorate media. Given the extensive use of these media in literature, which were

investigated by various techniques, nitrate, chloride and perchlorate media were chosen for this fundamental study to validate the applicability of the technique used in the present work. As discussed earlier, the Eu^{3+}/Eu^{2+} redox couple has been studied extensively in various electrolytes and has been used to explore new electrode materials. However the kinetic study has not been explored for nitrate media yet, and most often a mercury electrode was applied. To gain a better insight in the system, the electrochemical reduction of Eu^{3+} is investigated in three different media: perchlorate, chloride, and nitrate. Cyclic voltammetry and linear sweep voltammetry are performed using a glassy carbon rotating disk electrode under stationary or rotating conditions.

2. Experimental

2.1. Materials

$Eu(NO_3)_3{\cdot}6H_2O$ (99.9%), $EuCl_3.6H_2O$ (99.9%) and $Eu(ClO_4)_3$ in aqueous solution (50%) were purchased from Strem Chemicals, Inc. (Newburyport, USA). $Ca(NO_3){\cdot}4H_2O$ (≥ 99%), $CaCl_2{\cdot}6H_2O$ (98%) and $NaClO_4$ (≥ 98%) are purchased from Sigma-Aldrich (Overijse, Belgium). All products were used as received, without any further purification. Aqueous samples are prepared with Milli Q water (18.2 MΩ·cm at 25 °C).

2.2. Instruments and electrodes

A three-electrode electrochemical cell was used for the electrochemical reduction of europium. The potential was controlled using a Metrohm Autolab PGSTAT302N potentiostat in potentiostatic mode, controlled by Nova 2.1.5 software. The rotating disk electrode (RDE) experiments were conducted with an AUTOLAB RDE2 rotator with the rotation speed (100 to 10000 rpm), remotely controlled by the Nova software. A custom-made glass electrochemical cell with 100 mL inner capacity was used for the voltammetry tests. Prior to the

measurements, the solution was purged with argon gas. Experiments were conducted while an inert gas blanket was created by maintaining a continuous argon flow over the solution. The working electrode was a glassy carbon disk (Ø = 3 mm), the counter electrode was a coiled platinum wire (Ø = 1 mm) and the reference electrode was Ag/AgCl in 3 $mol.L^{-1}$ KCl. Prior to the measurements, the electrodes were cleaned first with 3 $mol.L^{-1}$ HNO_3, and then methanol. Solutions containing 10 $mmol.L^{-1}$ Eu^{3+} in 0.1 $mol.L^{-1}$ nitrate, perchlorate or chloride media were used as electrolytes. Higher concentrations of the electrolytes were avoided due to inhibition occurring on the working electrode.

3. Results and discussion

3.1. Cyclic voltammetry

Cyclic voltammetry (CV) was used to investigate the redox behavior of Eu^{3+} / Eu^{2+} in aqueous nitrate, chloride and perchlorate solutions, as well as to determine the reduction potentials as a function of the electrolyte composition. These experiments were performed using 10 $mmol.L^{-1}$ of Eu^{3+} salt containing the same anion as the electrolytes. The electrolyte concentrations were 0.1 $mol.L^{-1}$ for nitrate and chloride, and 1 $mol.L^{-1}$ for perchlorate media. The voltammograms were recorded in various scan rates in range 10 – 1000 $mV.s^{-1}$. The blank electrolytes were measured as well to validate that the electrochemical activity was originating uniquely from Eu^{3+} complexes (ESI Fig 1, Fig 2 and Fig 3).

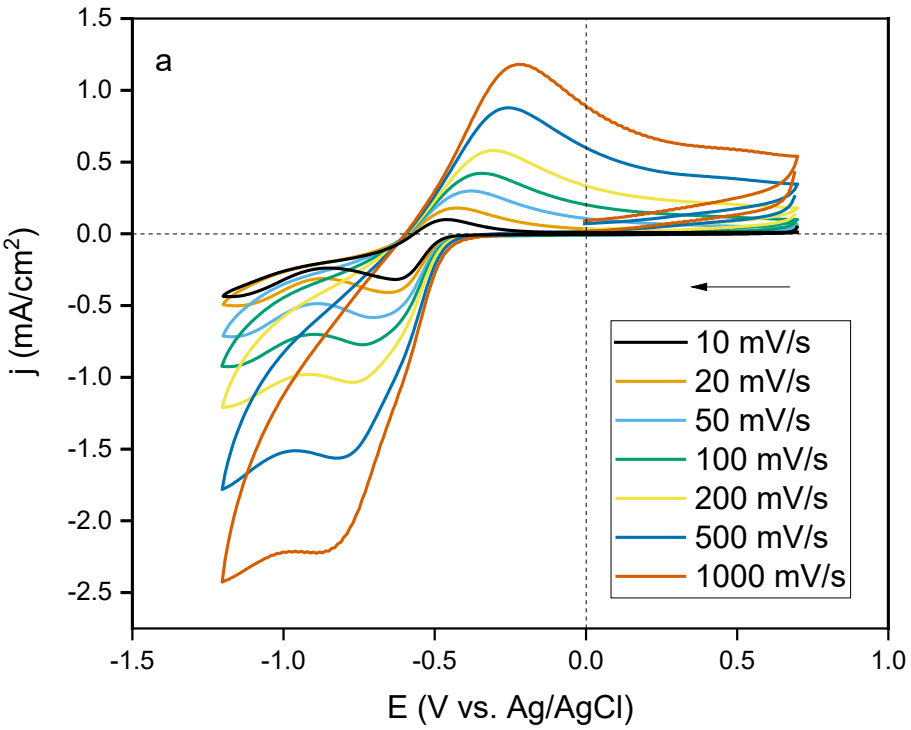
The influence of complexation in these electrolytes can be mainly explained by the change in hydration number and the inner/outer sphere coordination environment resulting in different reduction potentials. The formal reduction potential of a redox compound is affected by the interaction with ligands, i.e. the coordination of Eu^{3+} and Eu^{2+} and is a function of the ligand dissociation constants [41]. In addition, changing the electrolyte concentration leads to a

considerable difference in activity, ionic strength and hydration of the ions in solution, thus changing their inner coordination sphere. Europium ions are strongly hydrated in aqueous media because of their high charge densities, with the highest charge density for trivalent europium, which is known to be coordinated by 8 to 9 water molecules, whereas divalent europium is coordinated by 7 to 8 water molecules. Chloride and nitrate show only modest levels of association with lanthanide ions in aqueous solutions, mostly in the form of double-solvent-separated ion pairs. Therefore, they are found to predominantly form outer-sphere complexes, even at high salt concentrations. Thus, Eu^{3+} and Eu^{2+} ions in aqueous media can be considered fully hydrated ions.

The reduction of Eu^{3+} to Eu^{2+} was achieved in the electrolytes consisting of nitrate, chloride and perchlorate ions in quasi-neutral pH [21,31]. In the work of Van de Voorde *et al.* [21], both chemical and electrochemical reduction of Eu^{3+} to Eu^{2+} were performed at the pH of the solutions between 4 and 6.5 to avoid re-oxidation of Eu^{2+} by H^+ as well as the pH would be sufficiently low to prevent hydrolysis of Eu^{3+}. In addition, Rabockai *et al.* [29] discussed the influence of pH on the reduction of europium pair in 1 $mol.L^{-1}$ $NaClO_4$ in the presence of formamide using chronoamperometry on mercury electrode. It was reported that the pH effect was absent when solutions containing more than 70% formamide at all concentrations of Eu^{3+} were used, indicating that the reversibility of the reaction was independent on pH. However, at low concentrations of formamide (0 – 30%), the calculated kinetic parameters showed that the reaction was quasi-reversible, and mainly the anodic reaction was influenced more by pH compared to the cathodic process [29]. In the current work, based on these information, the pH of the solutions were kept ~4 and not further manipulated.

Fig. 1, Fig. 2, and Fig. 3 show the cyclic voltammograms of Eu^{3+} in perchlorate, nitrate and chloride media as a function of the potential sweep rate at a glassy carbon disk electrode. In all three media, a linear relationship between the cathodic peak currents and scan rate was observed, indicating a diffusion-controlled charge transfer. When the peak separation potentials are plotted as a function of potential sweep rate in logarithmic scale, as can be seen in Fig. 4, a linear relationship (with $0.991 \leq R^2 \leq 0.996$) is found for all electrolytes.

Only minor differences in the peak potentials at different electrolyte solutions were observed, as can be seen in Fig. 1, Fig. 2, and Fig. 3. At a sweep rate of 50 $mV.s^{-1}$, the cathodic peak potentials (E_p^c) are: -0.65, -0.68 and -0.68 V vs. Ag/AgCl, whereas the anodic peak potentials (E_p^a) are -0.40, -0.44 and -0.38 V vs. Ag/AgCl for perchlorate, nitrate and chloride media, respectively. The differences between the cathodic and anodic peak potentials are given in Table 1. Since these differences are larger than 59 mV in all media, and the E_p values change as a function of the scan rate, the reduction reaction in these electrolytes can be considered as being quasi-reversible.



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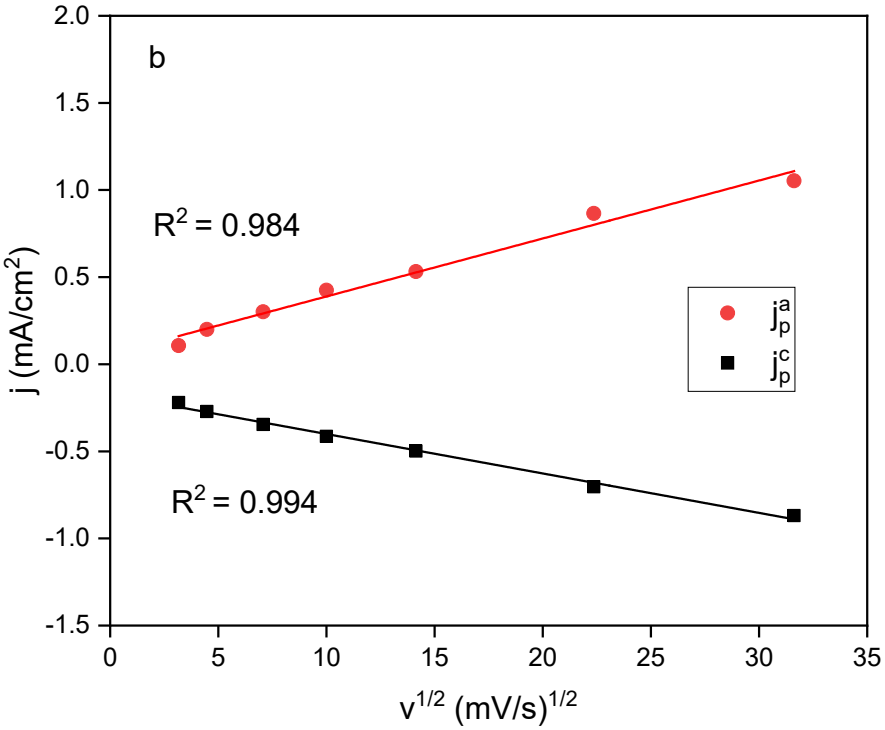

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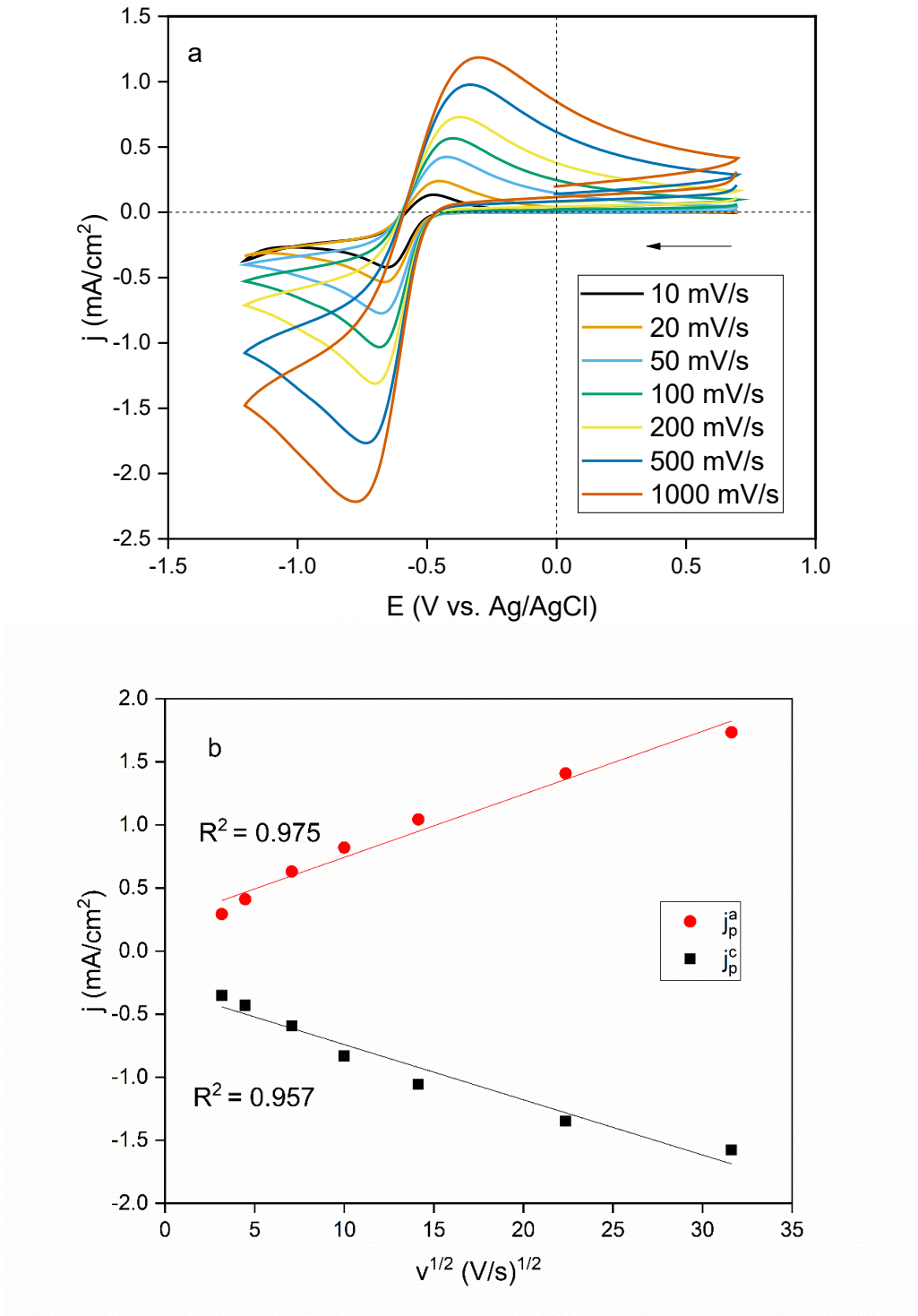
189 Fig. 1. a) Cyclic voltammograms (second cycles) of 10 mmol.L^{-1} Eu^{3+} in 1 mol.L^{-1} $NaClO_4$ at various scan rates
190 between 10-1000 mV/s b) Linear correlation of anodic and cathodic peak densities with respect to the square
191 root at these scan rates.



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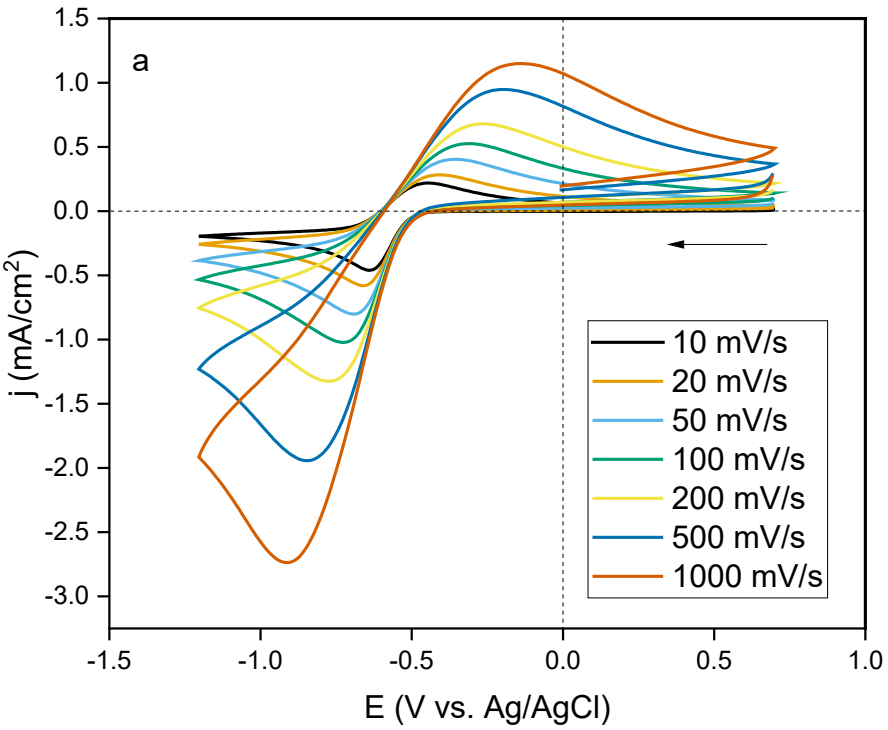
193 Fig. 2. a) Cyclic voltammograms (second cycles) of 10 mmol.L^{-1} Eu^{3+} in 0.1 mol.L^{-1} $Ca(NO_3)_2$ at various scan rates
194 between 10-1000 mV/s b) Linear correlation of anodic and cathodic peak densities with respect to the square
195 root at these scan rates.



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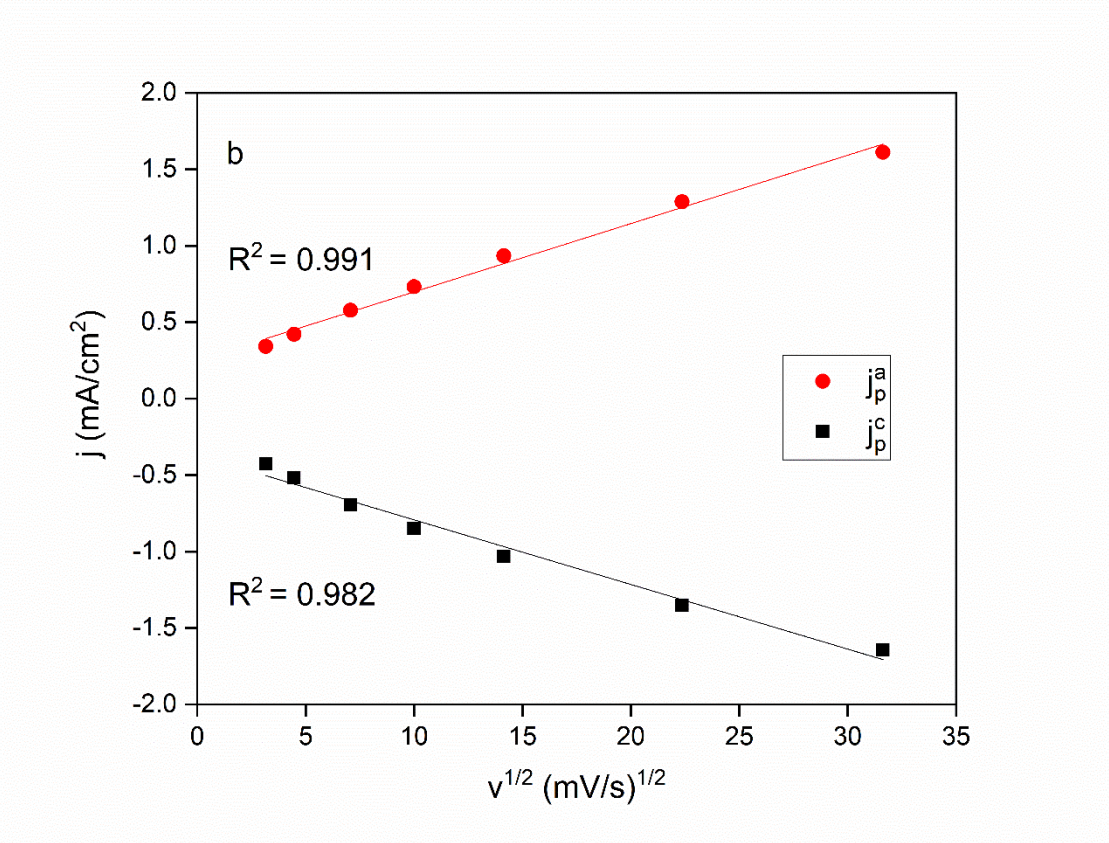

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198 Fig. 3. a) Cyclic voltammograms (second cycles) of 10 mmol.L^{-1} Eu in 0.1 mol.L^{-1} $CaCl_2$ at various scan rates
199 between 10-1000 mV/s b) Linear correlation of anodic and cathodic peak densities with respect to the square
200 root at these scan rates.

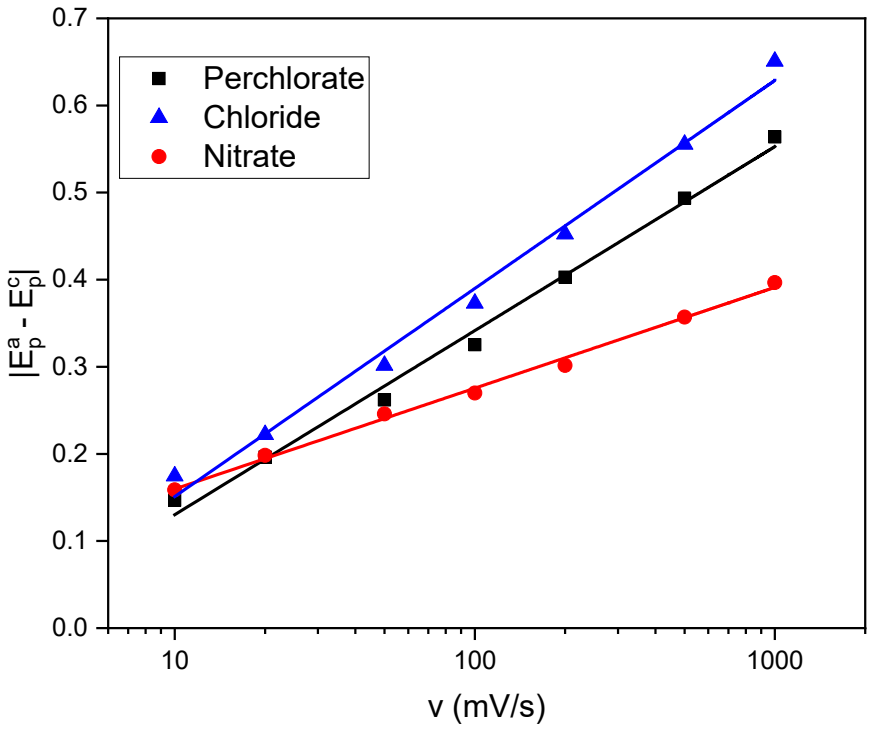


Fig. 4. Peak separation potentials of 10 mmol.L^{-1} Eu^{3+} in 1 mol.L^{-1} perchlorate, 0.1 mol.L^{-1} chloride and 0.1 mol.L^{-1} nitrate media as a function of scan rate in logarithmic scale.

Table 1. Difference in anodic and cathodic potentials at 10 mV/s and diffusion coefficients of Eu^{3+}/Eu^{2+} reaction at different electrolytes.

Medium	ΔE_p (V vs. Ag/AgCl)	D x 10^6 (cm^2/s)	Reported D values x 10^6 (cm^2/s)
1 mol.L^{-1} $NaClO_4$	0.25	6.42	4.8 [42] 5.7 [30] 10 [33]
0.1 mol.L^{-1} $Ca(NO_3)_2$	0.25	25.3	-
0.1 mol.L^{-1} $CaCl_2$	0.30	23.2	-

In aqueous chloride and nitrate media, it was observed that varying the salt concentration resulted in a shift of the reduction potential, and the reduction reaction was found to be more favorable at higher electrolyte concentrations [21]. Although the electrolyte concentration was higher in perchlorate medium, the peak potentials differed only ± 20 mV from the other electrolytes. Among these, the reduction potential was the lowest in nitrate medium, similar to the observations made by Van de Voorde *et al.*, where the oxidation and reduction of europium in nitrate aqueous media consistently have the lowest values at all concentrations [21]. Furthermore, chloride and perchlorate anions do only weakly interact with Eu^{3+} ions in aqueous media, so that only outer-sphere complexes are formed. However, Eu^{3+} nitrate solutions exhibit properties that lie between the behavior of those of weakly complexing chloride and perchlorate ions and the more strongly complexing sulfate ion [43–46]. Therefore, Eu^{3+} and Eu^{2+} ions are hydrated in these electrolytes and they form dominantly outer-sphere complexes, resulting in similar reduction potentials (E_p^c of -0.65 V vs. Ag/AgCl in perchlorate, -0.68 V vs. Ag/AgCl in nitrate and -0.68 V vs. Ag/AgCl in chloride media) independently of the electrolyte.

The relationship between the peak current and the scan rate for reversible reactions, which is also valid for quasi-reversible reactions, is given by the Randles–Sevcik equation:

$$i_p^c = 0.496nFCAD^{1/2}\left(\frac{(\alpha n_\alpha)Fv}{RT}\right)^{1/2} \quad (1)$$

where i_p^c is the cathodic peak current (in amperes), n is the number of exchanged electrons, F is the Faraday constant (96485 C. mol^{-1}), C is the europium concentration (in $mol.cm^{-3}$), A is the electrode surface area (in cm^2), D is the diffusion coefficient (in cm^2s^{-1}), v is the potential sweep rate (in $V.s^{-1}$), α is the charge-transfer coefficient, n_α is the number of electrons transferred in the rate-determining step, R is the universal gas constant and T is

234 the absolute temperature (in K). In all electrolytes, the linear dependence of cathodic peak
235 current to the square root of the scan rate , shows that the reduction of Eu^{3+} in these solvents
236 is diffusion-controlled (Fig. 1, Fig. 2 and Fig. 3). In order to calculate the diffusion coefficients
237 in these electrolytes, the αn_α value was estimated by using the half-peak potential
238 relationship equation for irreversible systems:

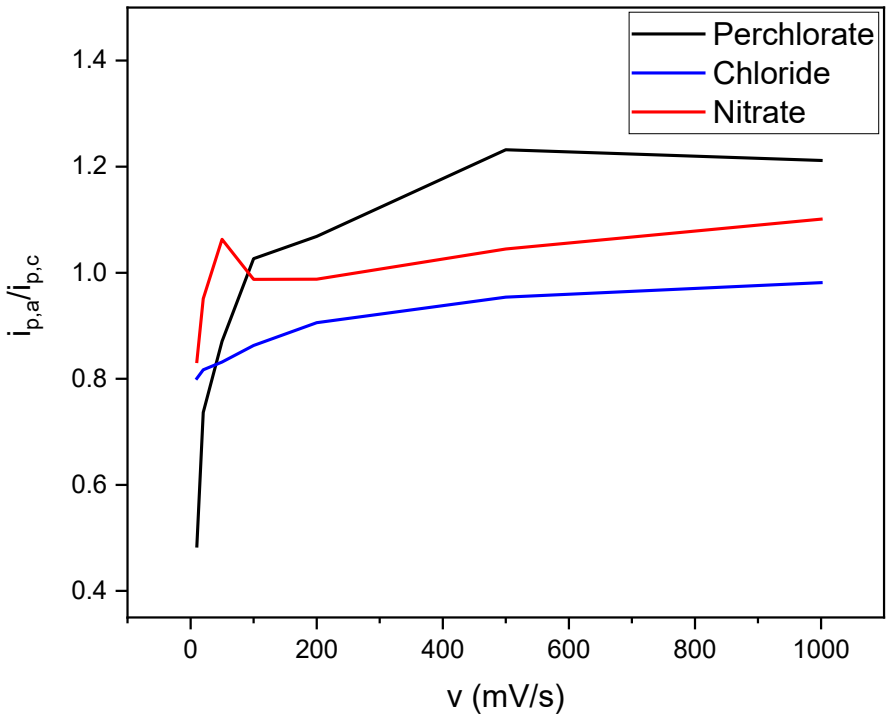
239 $$\left|E_p^c - E_{\frac{p}{2}}^c\right| = \frac{1.857\ RT}{\alpha n_\alpha F} \quad (2)$$

240 where $E_{\frac{p}{2}}^c$ is the cathodic half-peak potential. The calculated and reported D values can be
241 found in Table 1. The experimental values for the diffusion coefficient in perchlorate medium
242 are in close agreement with values reported in the literature, which were derived from
243 chronoamperometric techniques or polarography [30,38]. To the best of our knowledge, there
244 have been no studies reported in chloride or nitrate media yet, apart from the kinetic study in
245 2 $mol.L^{-1}$ HCl by Atanasyants *et al.* who reported mixed kinetics [28]. The diffusion coefficients
246 in all media are of the same order of magnitude, slightly higher in nitrate and chloride media.
247 The difference in the concentrations would impact the viscosity of these solutions. Thus, the
248 increase in the diffusion coefficient can be attributed to the decreasing viscosity in nitrate and
249 chloride media [47].

250

251 The reduction mechanism is further evaluated for all media by the ratio of the anodic peak
252 current to cathodic peak current with respect to scan rate (Fig. 5). In slower scan rates for the
253 perchlorate medium, the ratio is lower than 1, where with increasing scan rates the ratio
254 becomes closer to 1. This could suggest an irreversible chemical reaction paired with a
255 reversible electron transfer or an additional electrochemical redox couple overlapping the

potential range. In the chloride and nitrate media on the other hand, at all scan rates, the ratio seems to constant and close to 1, what could indicate a single reversible electron transfer. In addition, the linear correlation between $E_{p,c}$ vs. log(v) supports the EC mechanism for perchlorate medium [48]. Cyclic voltammetry simulations are performed to gain further insight in the possible electrochemical mechanisms of this redox couple using the CV Simulator tool developed by Brown *et al.* [49] (ESI Fig 4). The kinetic parameters of the simulations are presented in ESI Table 1 and show good general similarity to the experimental values obtained in this study via rotating disk experiments. The fittings were performed assuming an E mechanism, resulting in good agreement with the experimental voltammograms in chloride and nitrate media. In perchlorate medium, no good fit could be obtained for either a single E or EC mechanism. The contribution of a second electroactive species is therefore considered and could correspond to the H^+ reduction reaction. Steeman *et al.* [50] observed the interference of H^+ reduction at higher potentials in 1 M $NaClO_4$, overlapping with the Yb^{3+} reduction region. Similar to the observations in Yb^{3+} reduction, Eu^{3+} reduction in perchlorate electrolyte at moderate pH also result in the more prominent contribution of H^+ reduction at lower scan rates, which could explain the lower $i_{p,a}/i_{p,c}$ values at these scan rates.



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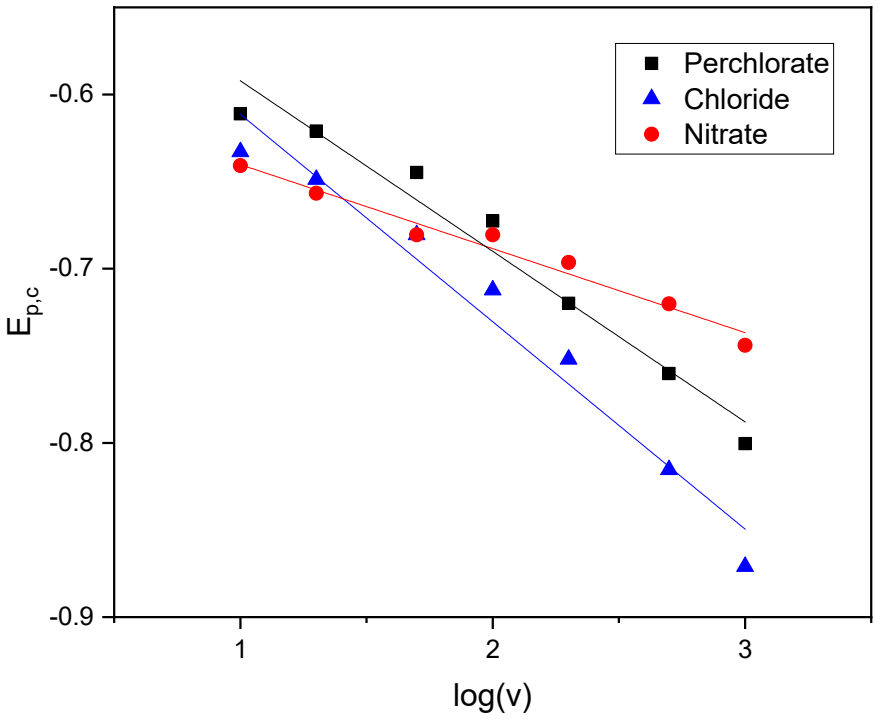
273 Fig. 5. Ratio of the anodic and cathodic peak currents of 10 mmol.L^{-1} Eu^{3+} in 1 mol.L^{-1} perchlorate, 0.1 mol.L^{-1}
274 chloride and 0.1 mol.L^{-1} nitrate media as a function of scan rate.



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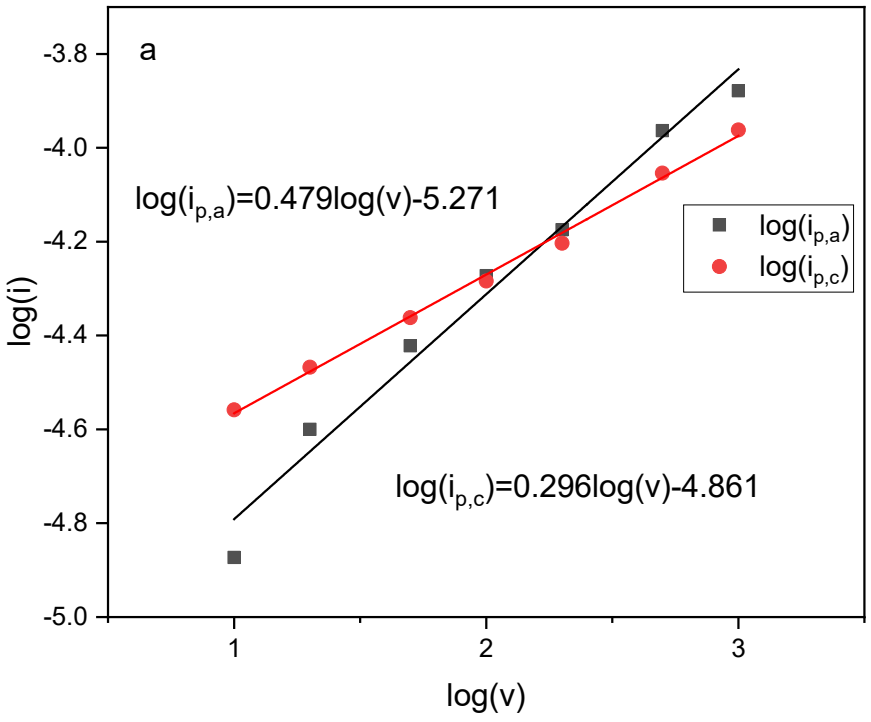
276 Fig. 6. E_p vs. log(v) graph for the voltametric peaks for perchlorate, chloride and nitrate media.



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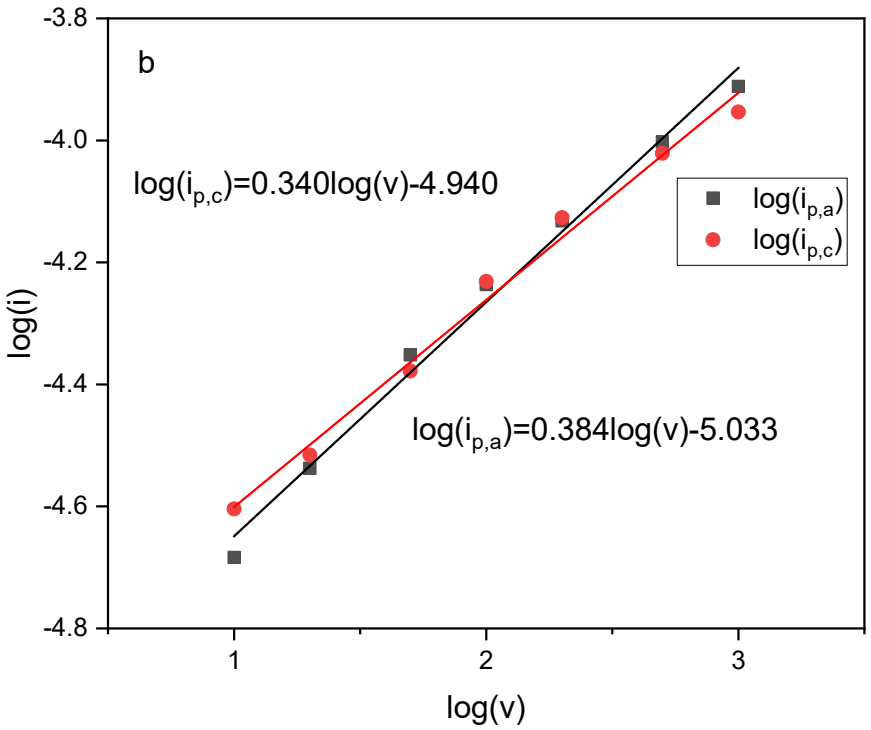

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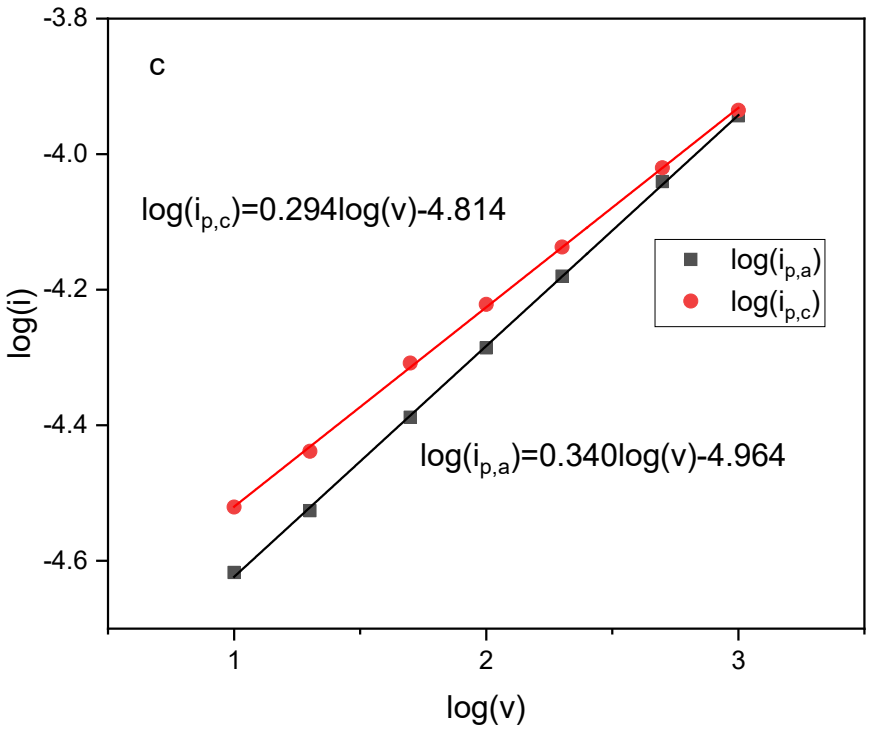

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280 Fig. 7. Log(i) vs. log(v) graph for the voltametric peaks for a) perchlorate, b) nitrate and c) chloride media.

281

The linear graphs of log(i) vs. log(v) in Fig. 7 show that the process is diffusion regulated, with charge transfer and mass transport both controlling the peak current [51]. The peak current ratio is discovered to be significantly larger than unity, which is consistent with the results and suggests that the system is quasi-reversible [47].

3.2. Linear sweep voltammetry at rotating disk electrode

Cyclic voltammetry is a valuable technique to qualitatively study the reactivity of compounds and to learn about the potential at which redox processes occur, the oxidation states, the number of electrons involved in the process, any possible chemical processes involved with the electron transfer etc. However, due to its non-stationary behavior and capacitive contributions involved, quantitative determination of kinetic parameters cannot be determined. Therefore, to further evaluate the kinetic parameters of the Eu^{3+} reduction reaction in perchlorate, nitrate and chloride media, linear sweep voltammetry at a rotating disk electrode (RDE) was used. Compared to polarography or chronoamperometry, rotating disk electrode experiments have advantages such as supplying more reliable mass transport conditions, quickly achieving steady-state electrode currents, a well-defined electrode surface for quantitative analysis and, as a result, higher sensitivity [52,53]. For these experiments, an in-house made water-jacketed three electrode glass cell with 100 mL inner volume was used. The solutions were purged with argon gas, at least for 30 minutes, before the experiment, and during the experiment an argon blanket was supplied to avoid oxidation of Eu^{2+} by air. In order to check the electrochemical activity of Eu^{3+}/Eu^{2+}, voltammograms were recorded at different rotation speeds.

In previous work of Van de Voorde *et al.*, a detailed parameter study was performed on the stability of Eu^{2+} as a function of the electrolyte composition, and it was found that the stability of Eu^{2+} increased at higher nitrate and chloride concentrations [21]. Based on these results, the initial experiments were conducted at 3 $mol.L^{-1}$ electrolyte solutions (ESI Fig 5 and Fig 6). However, at these high electrolyte concentrations, the voltammograms were not reproducible, and inhibition of the glassy carbon electrode was observed at higher rotation speeds. There are issues related with the use of nitrate salts as supporting electrolyte, due to the possible interactions with the electrode surface, anodic reactions of nitrate ions and complex formation with the ion of interest [54–56]. The inhibition of the electrode could also be explained by the selective adsorption of nitrate ions on the electrode which prevents the charge transfer reaction of europium. Therefore, the electrolyte concentrations was kept at 0.1 $mol.L^{-1}$ or 1 $mol.L^{-1}$ to obtain reliable results and to enable comparison of calculated kinetic parameters with literature data.

The dependence of current density on the electrode potential is presented in the linear sweep voltammograms in Fig. 5.a., Fig. 6.a. and Fig. 7.a. in chloride, nitrate and perchlorate media, respectively. These curves can be separated into three regions: the charge-transfer-limited region with initial exponential increase in current density, the mixed kinetics region where diffusion and charge transfer both contribute to the kinetics, and the mass-transfer limited plateaus. The kinetic analysis using a rotating disk electrode can be performed using two correlations in the respective regions: Levich and Koutecký-Levich analysis. The equations to calculate the kinetic parameters via these methods are given as:

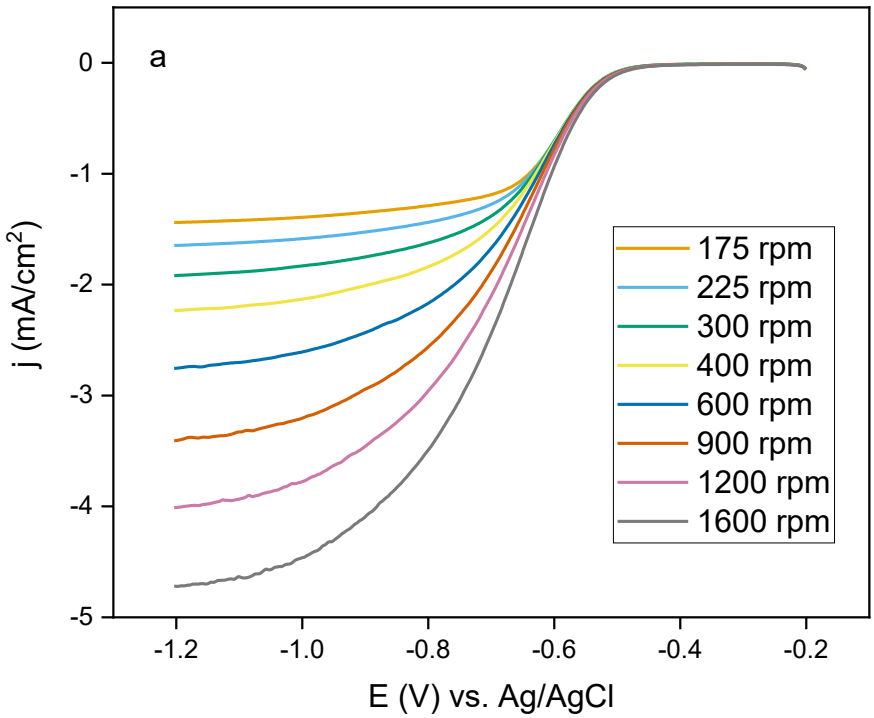
$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_l} = \frac{1}{i_k} + \frac{1}{B\omega^{1/2}} \quad (3)$$

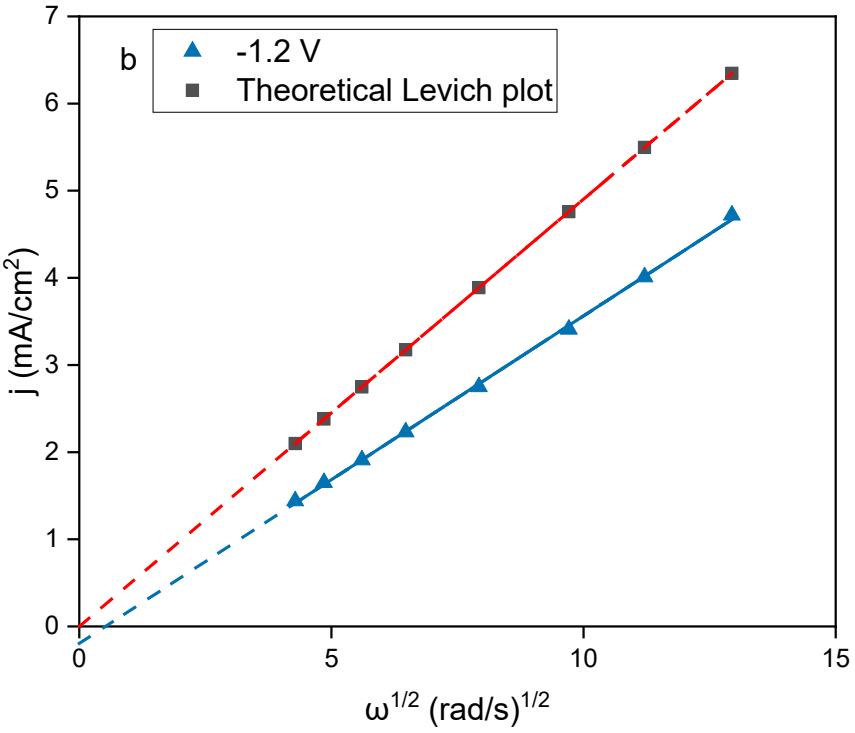
$$B = 0.62AnFD^{2/3}v^{-1/6}\,C \quad (4)$$

$$i_k = nFAkC \quad (5)$$

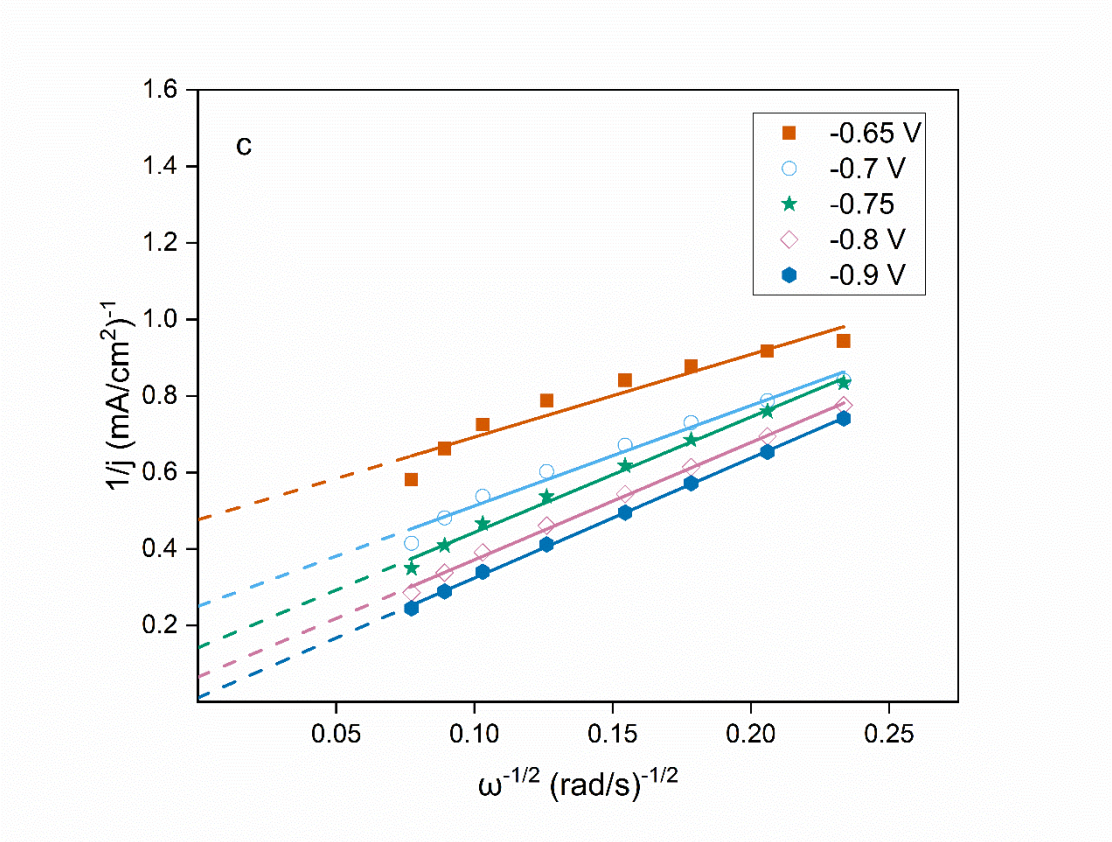
$$i_l = 0.62AnFD^{2/3}v^{-1/6}C\sqrt{\omega} \quad (6)$$

The variables for these equations are; n is the number of exchanged electrons, F is the Faraday constant (96485 C.mol^{-1}), C is the europium concentration (in mol.cm^{-3}), A is the electrode surface area (in cm^2), k is the rate constant for electron transfer (in cm.s^{-1}), D is the diffusion coefficient (in cm^2.s^{-1}), v is the potential sweep rate (in V.s^{-1}), α is the charge-transfer coefficient, n_α is the number of electrons transferred in the rate-determining step, R is the universal gas constant (8.314 J.mol^{-1}.K^{-1}), T is the absolute temperature (in K), ω is the angular frequency of rotation (rad.s^{-1}), ν is the kinematic viscosity of the electrolyte (cm^2.s^{-1}), i_k is the kinetic current and i_l is the limiting current (in A).

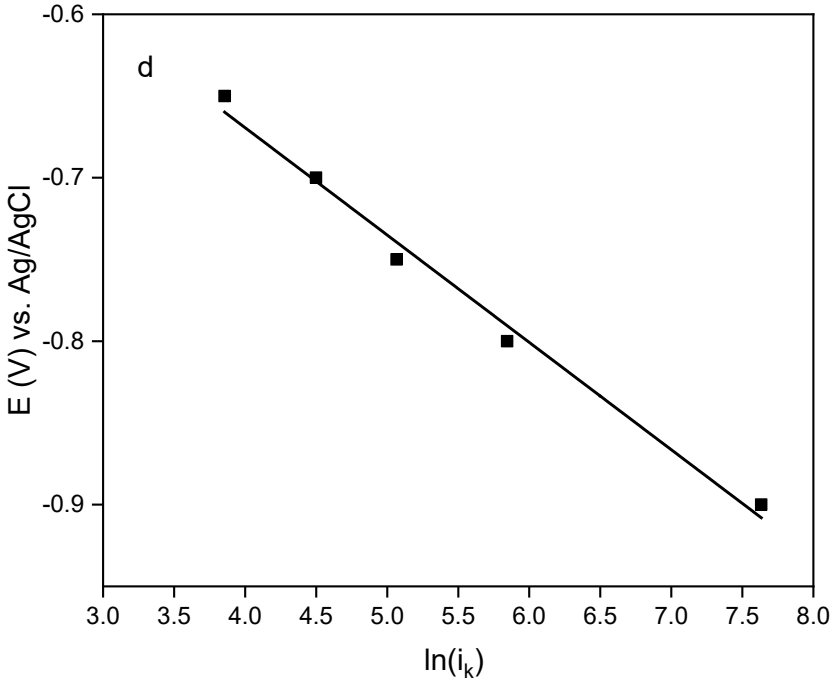



b
-1.2 V
Theoretical Levich plot
j (mA/cm^2)
$\omega^{1/2}$ (rad/s)$^{1/2}$
0
1
2
3
4
5
6
7
0
5
10
15

339

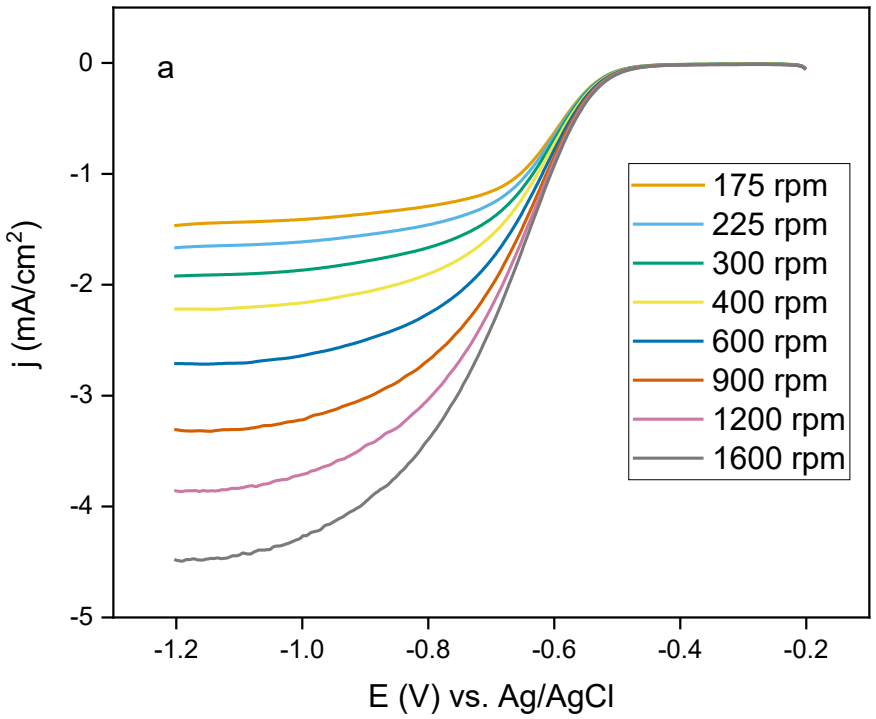

c
-0.65 V
-0.7 V
-0.75
-0.8 V
-0.9 V
1/j (mA/cm^2)$^{-1}$
$\omega^{-1/2}$ (rad/s)$^{-1/2}$
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
0.05
0.10
0.15
0.20
0.25

340

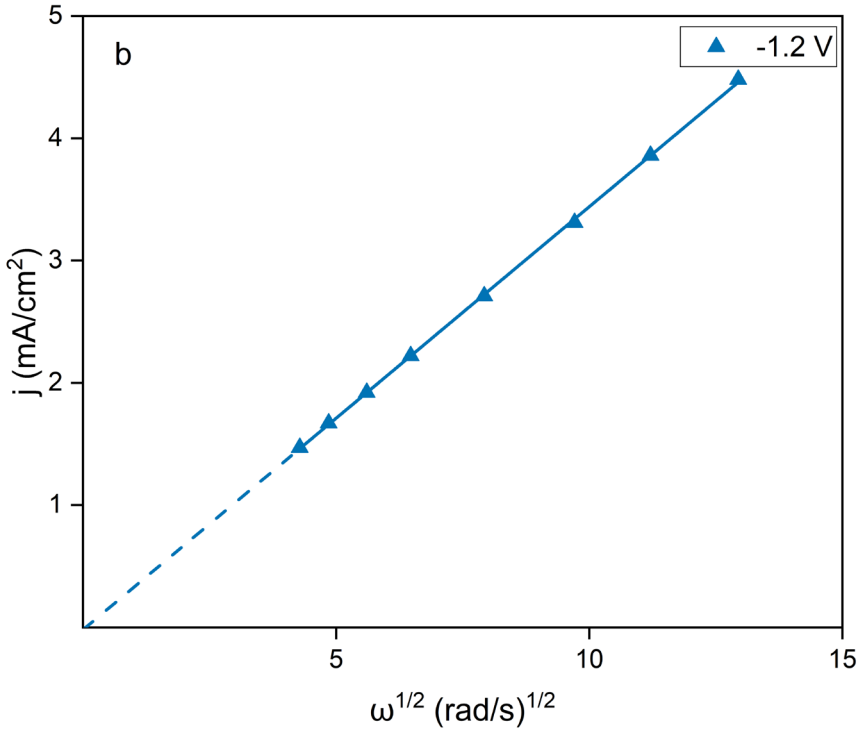


341

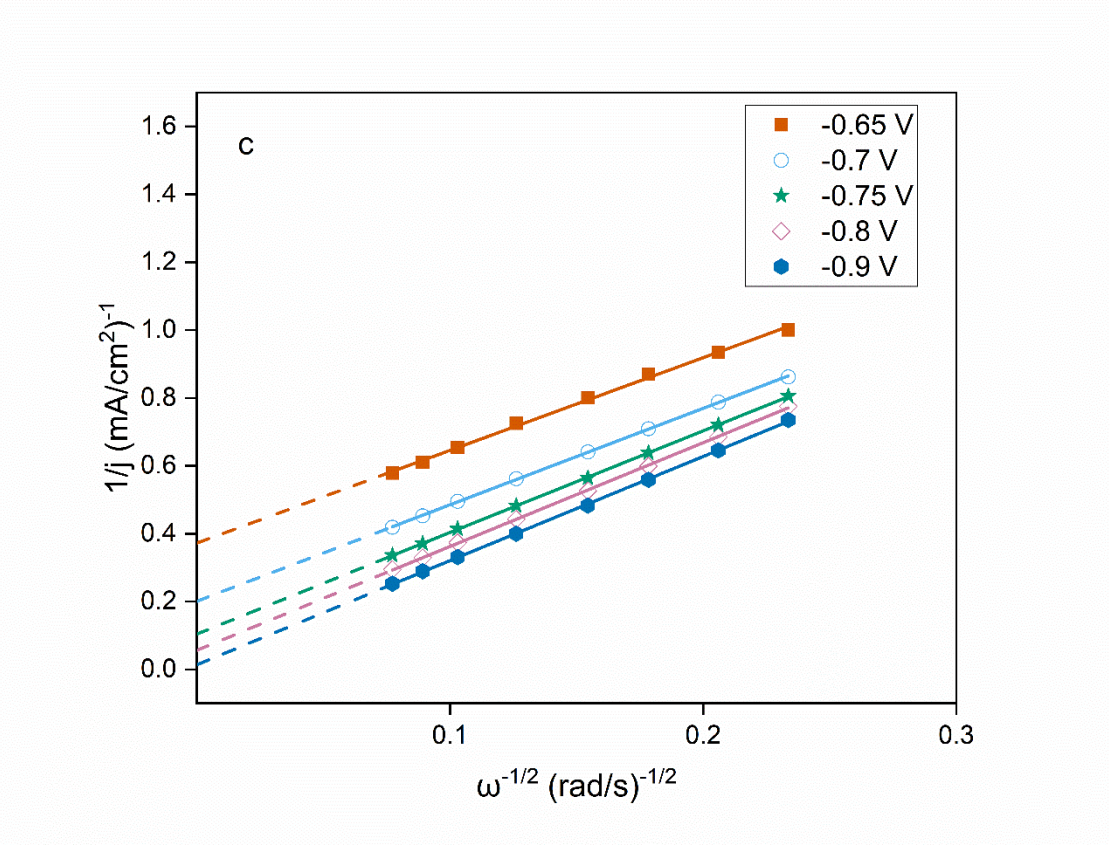
342 Fig. 8. a) Linear sweep voltammogram on a glassy carbon rotating disk electrode in 0.01 mol L^{-1} Eu^{3+} in 0.1
343 mol.L^{-1} $CaCl_2$ solution at a scan rate of 50 mV.s^{-1} for rotation speeds 175 – 1600 rpm b) Levich plot and c)
344 Koutecký – Levich plot at various potentials d) Tafel plot deducted from the Koutecký–Levich analysis


a
0
-1
-2
-3
-4
-5
j (mA/cm^2)
-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
E (V) vs. Ag/AgCl
175 rpm
225 rpm
300 rpm
400 rpm
600 rpm
900 rpm
1200 rpm
1600 rpm

345


b
-1.2 V
5
4
3
2
1
j (mA/cm^2)
5
10
15
$\omega^{1/2}$ (rad/s)$^{1/2}$

346



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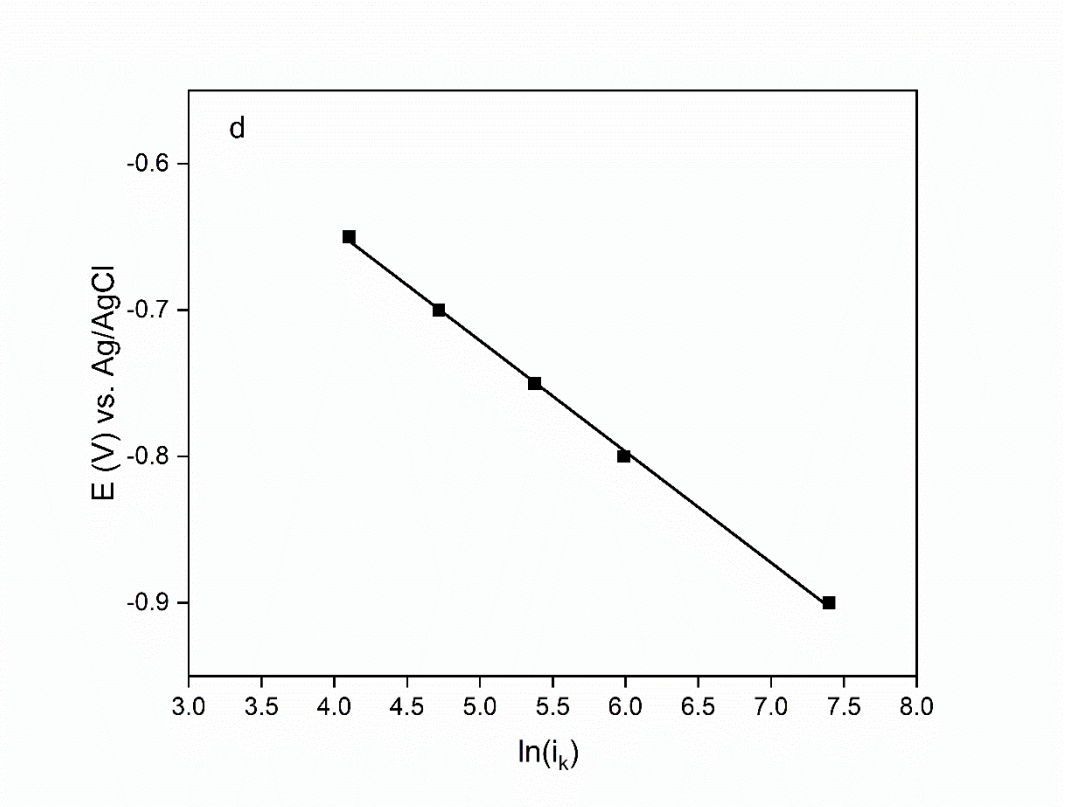
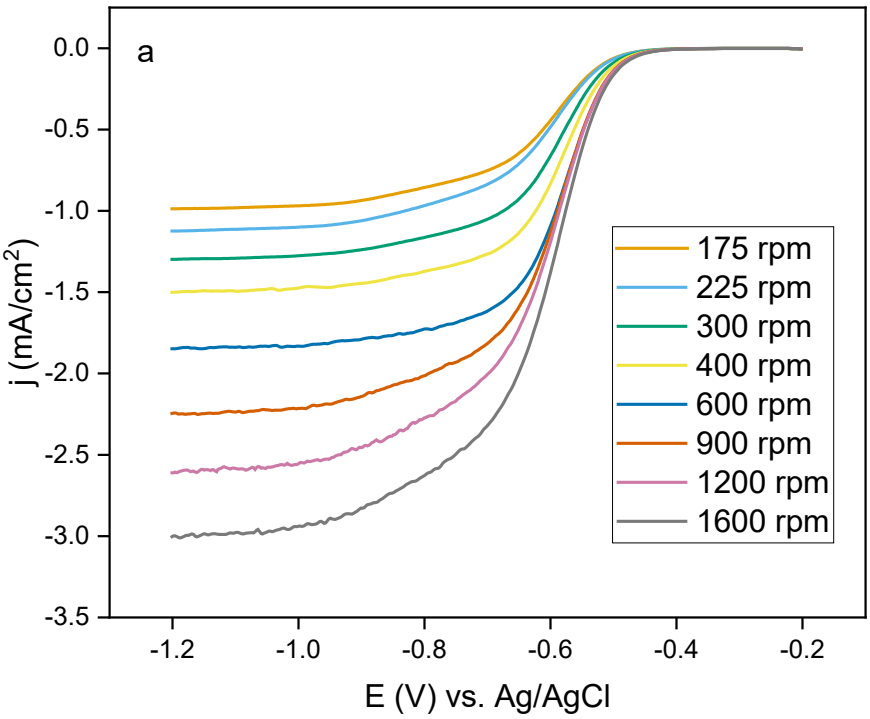


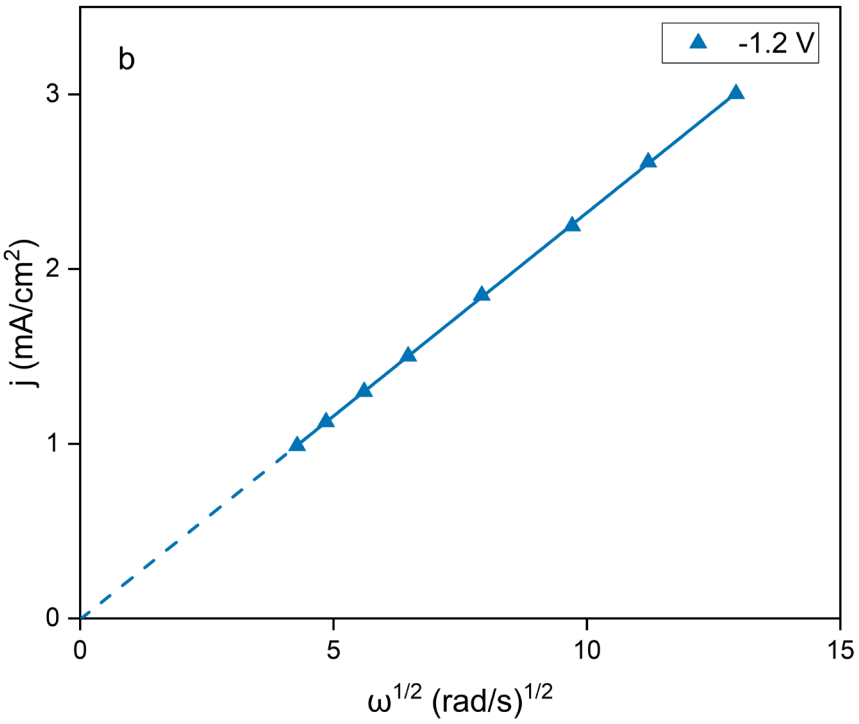
348

349

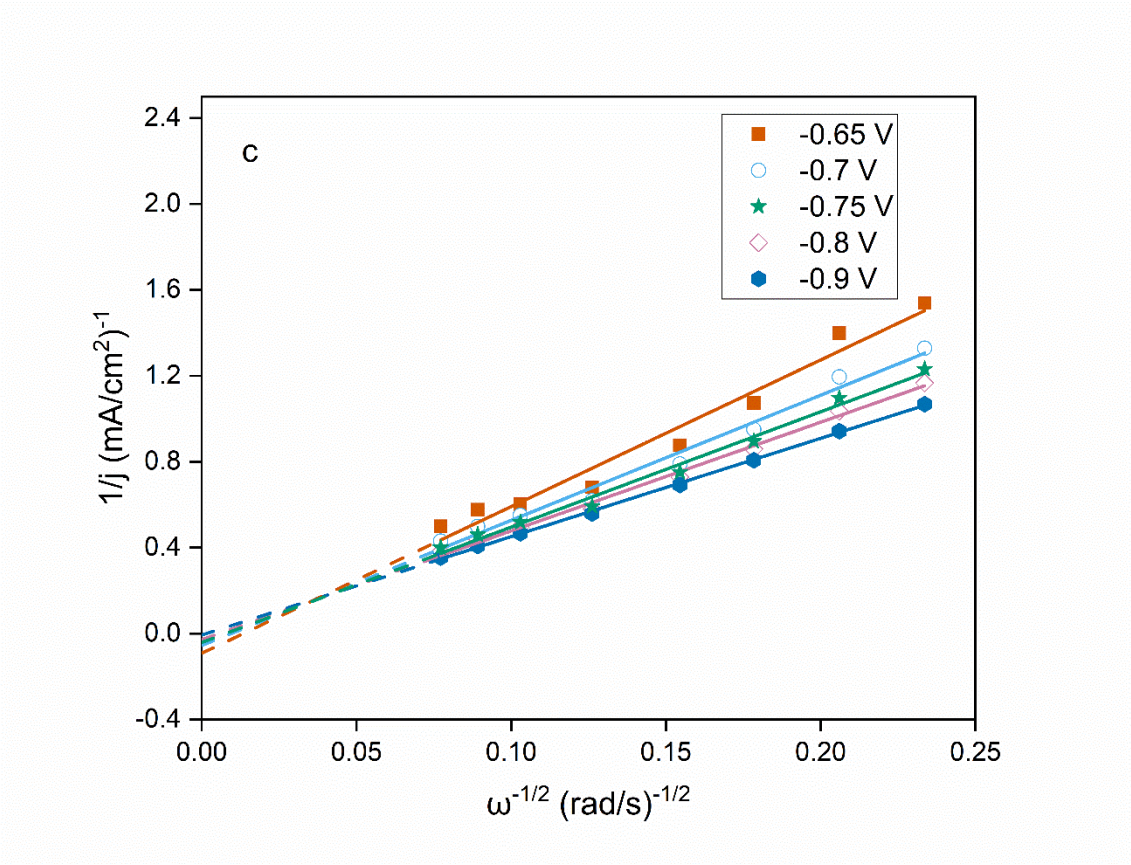
350 Fig. 9. a) Linear sweep voltammogram on a glassy carbon rotating disk electrode in 0.01 mol.L^{-1} Eu^{3+} in 0.1
351 mol.L^{-1} $Ca(NO_3)_2$ solution at a scan rate of 50 mV s^{-1} for rotation speeds 175 – 1600 rpm b) Levich plot and c)
352 Koutecký – Levich plot at various potentials d) Tafel plot deducted from the Koutecký–Levich analysis


a
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
j (mA/cm^2)
-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
E (V) vs. Ag/AgCl
175 rpm
225 rpm
300 rpm
400 rpm
600 rpm
900 rpm
1200 rpm
1600 rpm

353


b
-1.2 V
3
2
1
0
j (mA/cm^2)
0
5
10
15
$\omega^{1/2}$ (rad/s)$^{1/2}$

354



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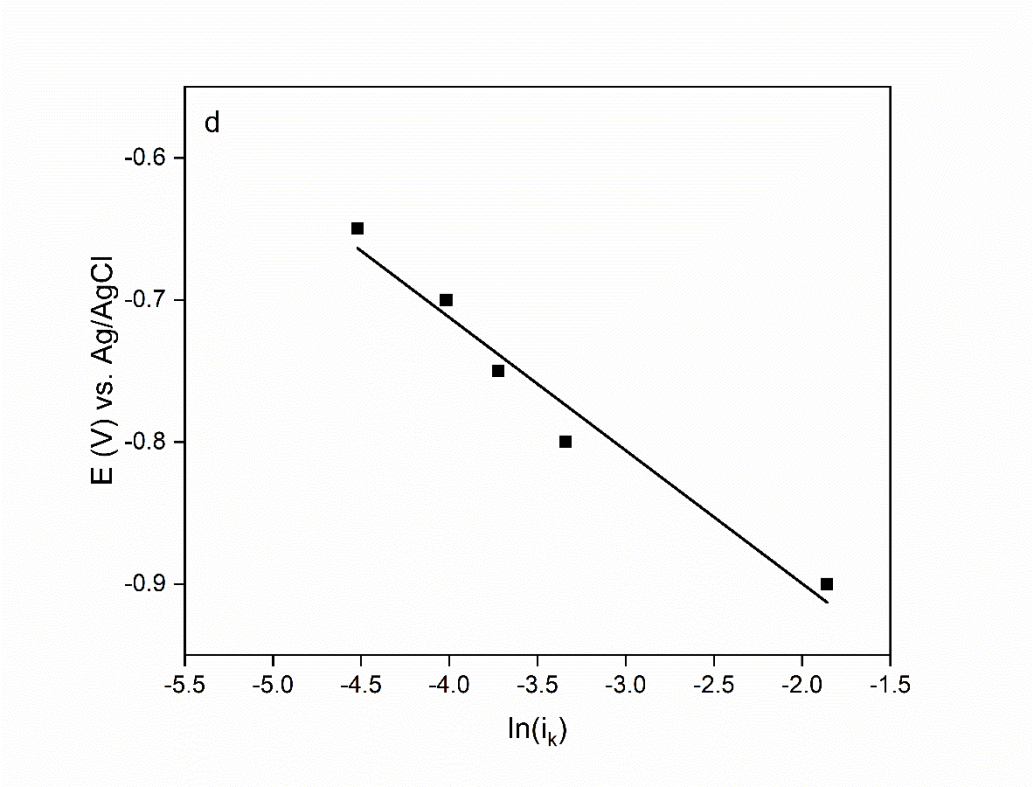

356

357

358 Fig. 10. a) Linear sweep voltammogram on a glassy carbon rotating disk electrode in 0.01 mol.L^{-1} Eu^{3+} in 1 mol.L^{-}
359 ^{1} $NaClO_4$ solution at a scan rate of 50 mV.s^{-1} for rotation speeds 175 – 1600 rpm b) Levich plot and c) Koutecký
360 – Levich plot at various potentials.

The Levich plots are presented in Fig. 5.b., Fig. 6.b., and Fig. 7.b., and were fitted by linear regression analysis, with the intercepts shown. Based on Eqn. 6, the slope of the Levich plot can be used to calculate the diffusion coefficients. These calculated values are given in Table 2. There is no deviation from the linearity in these plots, with linear fitting R^2 values ($R^2 \geq 0.999$), proving the mass transport regime at the limiting current. However, it is observed that in chloride medium due to the adsorption of Eu^{3+}ions rather than Eu^{2+} over the electrode surface, the experimental Levich plot deviates from the theoretical one. The kinematic viscosities for the electrolyte solutions were estimated by the literature values reported as 0.00899 $cm^2.s^{-1}$ for 0.1 $mol.L^{-1}$ $Ca(NO_3)_2$, 0.00896 $cm^2.s^{-1}$ for 0.1 $mol.L^{-1}$ $CaCl_2$, and 0.00917 $cm^2.s^{-1}$ for 1 $mol.L^{-1}$ $NaClO_4$ [21][52]. By using the Levich equation, the diffusion coefficients were calculated with the assumption that the reaction is a one-electron process. For perchlorate medium, the diffusion coefficient values are in the same order of magnitude compared to the earlier calculations from cyclic voltammetry, where the values are slightly higher in less concentrated nitrate (10.7×10^6 $cm^2.s^{-1}$) and chloride (11.71×10^6 $cm^2.s^{-1}$) solutions compared to the perchlorate media (7.28×10^6 $cm^2.s^{-1}$). A variation is observed between diffusion coefficients calculated based on cyclic voltammetry (Randles-Sevcik and simulation) and rotating disk electrode. Values are all in the same order of magnitude and the ratios between the investigated media are consistent over all applied methods. Koutecký-Levich analysis was performed to calculate the rate constant for the charge transfer in all media, and the results are summarized in Table 2.

Table 2. D, α and k values calculated based on Levich and Koutecký-Levich analysis.

Medium	D x 10^{6} (cm^2/s)	k (cm/s)	k (cm/s)*
1 $mol.L^{-1}$ $NaClO_4$	7.28	1.13 x 10^{-4}	1.6 x 10^{-4} [38] 2.4 x 10^{-4} [29]
0.1 $mol.L^{-1}$ $Ca(NO_3)_2$	10.7	2.88 x 10^{-3}	-
0.1 $mol.L^{-1}$ $CaCl_2$	11.71	2.18 x 10^{-3}	-

*These values are obtained from literature reports.

The rate constants were calculated by using equations 3, 4 and 5, where the intercept of the Koutecký-Levich plot equals to the inverse of the kinetic current. The value for the reference perchlorate medium was calculated as 1.13 x 10^{-4} $cm.s^{-1}$, which is very similar to the literature values [29,38]. The calculated value being similar to the literature validates that this method is applicable to the aqueous electrolytes that are studied. It was observed that in nitrate and chloride media, the rate constant was ten times larger than in perchlorate medium with 2.88 x 10^{-3} $cm.s^{-1}$ in nitrate and 2.18 x 10^{-3} $cm.s^{-1}$ in chloride solutions. These differences can be explained by the differences in hydration at different concentrations. In addition to the differences in hydration of the europium ions and viscosity of the solutions due to the electrolyte concentration, for nitrate medium, reduction products of nitrate might influence the electrode reactions [21,56].

According to the literature data [27,31], the rate of the electrode process in chloride and perchlorate solutions should be similar (k ~ 10^{-4} $cm.s^{-1}$) since inner-sphere complexation and anion adsorption are not prominent, whereas in nitrate medium an opposite observation is made. Additionally, it was demonstrated that the first coordination sphere of Eu^{3+} in perchlorate and chloride solutions solely contains water molecules, even at very high salt

concentrations, whereas $EuNO_3^{2+}$ can also form in nitrate medium [43]. Based on a study by Kinard *et al.* [27], the reversibility as a function of supporting electrolytes shows the following trend: ClO_4^- < Cl^- < NO_3^- < Br^- < I^-< SCN^- and the outer-sphere complexes give the same limiting current, indicating similarities in reduction mechanism within this series. Although the differences in complexation could impact the kinetics at higher concentrations, based on these results, the differences in rate constants and diffusion coefficients can be attributed rather to the concentration of these electrolytes.

4. Conclusions

The kinetics of the Eu^{3+} to Eu^{2+} reduction reaction were studied in perchlorate, nitrate and chloride media using cyclic voltammetry and linear sweep voltammetry on a rotating disk electrode. The perchlorate medium was selected as a reference condition to explore the methodology, and the kinetics study in the nitrate and chloride electrolytes are explored, to the best of our knowledge, for the first time. The diffusion coefficients were calculated by both cyclic voltammetry and Levich analysis, and these values are in the same order of magnitude and in a good agreement with literature data based on polarographic methods. The reaction is quasi-reversible in all the electrolytes under these chosen experimental conditions, which is confirmed by the difference in peak separation potential. It was proposed that the hydrogen reduction reaction occurs at higher potentials in the perchlorate media and partially overlaps with Eu^{3+} reduction. Koutecký-Levich analysis was performed to retrieve information on the kinetic parameters of the Eu^{3+} reduction for the first time. The rate constants in the different media amount to 1.13×10^{-4} $cm.s^{-1}$ for perchlorate, 2.88×10^{-3} $cm.s^{-1}$ for nitrate and 2.18×10^{-3} $cm.s^{-1}$ for chloride. Hence, the values for nitrate and chloride differ one order of magnitude. These minor differences in the nitrate and chloride electrolytes can be attributed to

differences in concentration and viscosity rather than to the complexation or sluggish kinetics, since the concentrations were low.

Acknowledgements

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