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Electrochemical Reduction of Europium(3+) at Increasing Concentrations of Different Salts. Part I. Voltammetric Measurements

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Under the influence of spectroscopic results, which seem to indicate an increase of the hydration number at a decreased water activity in perchlorate and (some) chloride solutions, a reinvestigation of europium(3+) electrochemical reduction in different electrolytes was performed. Influences of the mentioned anions on the electrode response in square wave voltammetry are really similar if the peak potential shift and peak height decrease are followed in dependence on the electrolyte concentration. Results in nitrate, bromide and iodide media differ significantly due to the europium(3+) inner sphere complexation or change of the electrode kinetics in the presence of adsorbed anions. It remains questionable if the corresponding results (along with those of dc polarography) could be used for diagnostic purposes in solutions of europium(3+) and less common electrolytes, *i.e.*, for distinguishing the processes that include »inert«, surface active or complex forming anions.

INTRODUCTION

An increasing interest in the chemistry of lanthanides has been noticed during the last two decades.[1,2] Europium seems to be the most »popular« among them due to the »anomalous« hydration of Eu^{3+}, [3–6] luminescent[1,7–10] and catalytic[11,12] properties of its complexes, stability of 2+ oxidation state, *etc*.

According to different studies,[3–6] based on luminescence and Raman spectroscopy, the hydration number of Eu^{3+} seems to increase, from 8 to 9, 10 or even more, with decreasing water activity. Lis and Choppin,[4] however, interpreted the corresponding experimental results in terms of an increased interaction between the metal ion and the water molecules in its primary coordination sphere as a result of reduced secondary hydration.

Taking into account that in this type of studies the hydrated ions are often treated as complexes, formation of higher species at a lower ligand concentration is something completely opposite to all known models and relationships. For this reason, the problem should be additionally studied using other independent methods. Voltammetric and other electrochemical techniques often used in hydration studies of free metal ions[13–15] are of limited use here because Eu^{2+} rather than the amalgam appears as a reduction product and only the difference between hydration numbers of the oxidized and reduced forms can be calculated assuming the reversibility of the electrode process in the ligand concentration range of interest.[16]

Unfortunately, the only obvious conclusion arising from the published electrochemical results,[17–27] obtained in aqueous[17–25] and nonaqueous[26,27] media, points to the irreversibilization of the reduction process with increasing the electrolyte concentration, especially if the corresponding anions are not specifically adsorbed. The effect was ascribed to the changes of the double layer structure[17, 23] but the application of the corresponding corrections was not always quite successful.[19] Although discussed in some papers,[21,22] the role of europium hydration in the kinetics of the reduction process has never been really confirmed. Therefore, it remains questionable if the »strange« results obtained by spectroscopic and voltammetric techniques have, at least partly, the same origin or, in other words, if it is possible to find an »electrochemical equivalent« of the decreased luminescence life time at increased electrolyte concentrations.

The whole problem of europium(3+) hydration is not of pure academic interest because classical complexation studies usually start with characterization of the free metal ion in an aqueous (electrolyte) solution. In addition, the water remaining in the coordination sphere after complex formation and interaction of such a complex with the solvent are of the utmost importance. This is because water molecules could significantly reduce the intensity of emission of luminescent europium complexes, which are nowadays treated as important probes in biochemistry.[1]

In this paper, the electrochemical reduction of Eu^{3+} at increasing concentrations of different electrolytes (*i.e.*, decreasing water activity) will be reinvestigated and correlated with the literature data on the changes in europium(3+) hydration. For this purpose, square wave voltammetry (SWV), as a method extremely sensitive to changes in the character of the electrode process,[28,29] will be used along with sampled dc polarography.

EXPERIMENTAL

All solutions were prepared from reagent grade chemicals and doubly distilled water.

Voltamograms were recorded using the µAutolab System (Eco Chemie, Utrecht) attached to a static mercury drop electrode PAR 303 (Princeton Applied Research.). Platinum wire served as a counter electrode while all potentials were given with respect to the saturated Ag/AgCl (NaCl) reference electrode.

Before each measurement, the solution in the polarographic cell was deaerated with high purity nitrogen for 20 minutes and a nitrogen blanket was maintained over the surface during the measurements. The room temperature was maintained in the range 24 ± 1 °C.

In general, two types of experiments were performed. In one series, starting with the europium solution in 0.01 mol L^{-1} $HClO_4$, the concentration of the chosen electrolyte was gradually increased (at a constant level of the dissolved metal and at constant acidity). In the other series, the ionic strength was also fixed but two electrolytes were present in different proportions.

RESULTS AND DISCUSSION

Reduction in Dilute Perchloric Acid

As all the measurements at increased salt concentrations were performed in solutions containing 0.01 mol L^{-1} $HClO_4$, it was important to characterize europium(3+) reduction in this medium. Although low levels of perchloric acid (pH = 1–3) do not influence the rate of the electrode process,[24] the results obtained at the chosen electrolyte concentration could be complicated by ohmic drop effects and incompletely suppressed migration processes. Anyway, such measurements could be a good starting point if one wished to study the influence of a gradually increasing salt concentration on the process of interest.

At an increasing SW frequency (f = 10–200 s^{-1}), europium(3+) reduction current (i_p) increases, its peak potential (E_p) shifts negatively (Figure 1A) whereas the change of the half-width is not pronounced. At both metal concentrations applied (0.1 and 0.5 mmol L^{-1}), the ratio of the peak currents at the highest and lowest frequencies $(i_p)_{200} / (i_p)_{10} = 3.1$. If such results are presented in the i_p *vs.* $f^{1/2}$ form, curves are obtained instead of straight lines. The peak potential shift defined as $(E_p)_{10} - (E_p)_{200}$ is, however, more pronounced at the higher europium level (34 *vs.* 18 mV). If $f > 200$ s^{-1} is applied, decreasing and broadening of the voltammetric signal occur together with its translation along the *y*-axis. Finally, the whole response becomes poorly pronounced. (Figure 1B). All these results belong to the group of ohmic drop effects[30,31] whereas, because of the high electrolyte to analyte concentration ratio, migration seems to be unimportant.

It was demonstrated[30] (by model calculations) that the influence of IR drop could be represented by the complex

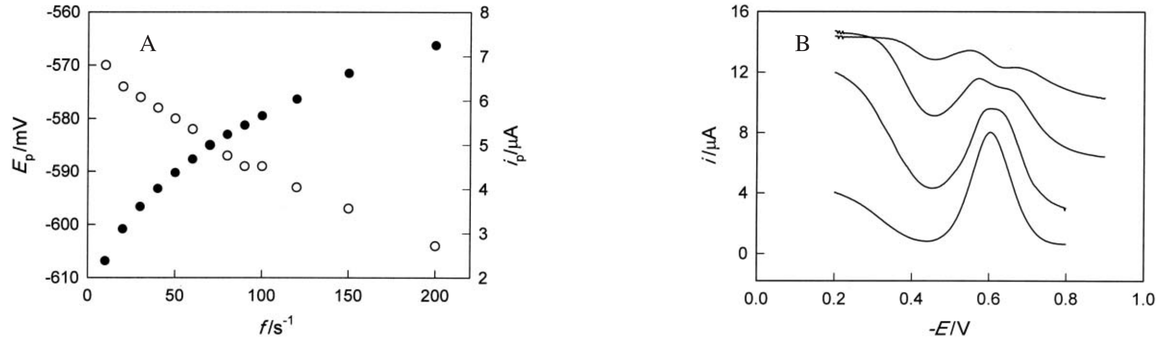

Figure 1. (A) Dependence of europium(3+) peak height (●) and potential (○) on SW frequency. Metal concentration: 0.5 mmol L^{-1}, electrolyte: 0.01 mol L^{-1} $HClO_4$, SW amplitude: 50 mV, scan increment: 2.5 mV. (B) Voltamograms recorded at high frequencies (in the ascending order f = 200, 300, 400 and 500 s^{-1}).

dimensionless resistance argument $\rho = (nF)^2 S c_{ox} (Df)^{1/2} R_\Omega / RT$ where S denotes the electrode surface area, c_{ox} is the bulk concentration of the oxidized form, R_Ω is ohmic resistance while other symbols have their usual meaning. At low values of ρ the SWV response is virtually unaffected, but for $\rho \geq 1$ it becomes changed and finally totally disturbed. It follows that the results obtained at two different europium concentrations in the studied system cannot be identical because they reflect the change in the ρ value.

If sampled-current polarography is applied instead of square wave voltammetry, the half-wave potential is virtually constant (–559 ± 2 mV) in the drop-time range 0.5–5 s while the slope corresponds to the one electron diffusion controlled process.

Reduction in Sodium Perchlorate Solutions

Taking into account that characteristics of the europium(3+) reduction signal in 0.01 mol L^{-1} $HClO_4$ depend on the SW frequency and the level of dissolved metal, the influence of increasing $NaClO_4$ concentration was followed at the two mentioned europium concentrations (0.1 and 0.5 mmol L^{-1}) and two SW frequencies (20 and 100 s^{-1}).

Regardless of the metal concentration or the SW frequency applied, the peak height starts to decrease at a very low (<10^{-2} mol L^{-1}) sodium perchlorate level to reach a constant value at the concentration of about 1 mol L^{-1} (Figure 2), which corresponds to about 30 % of the current measured in 0.01 mol L^{-1} $HClO_4$.

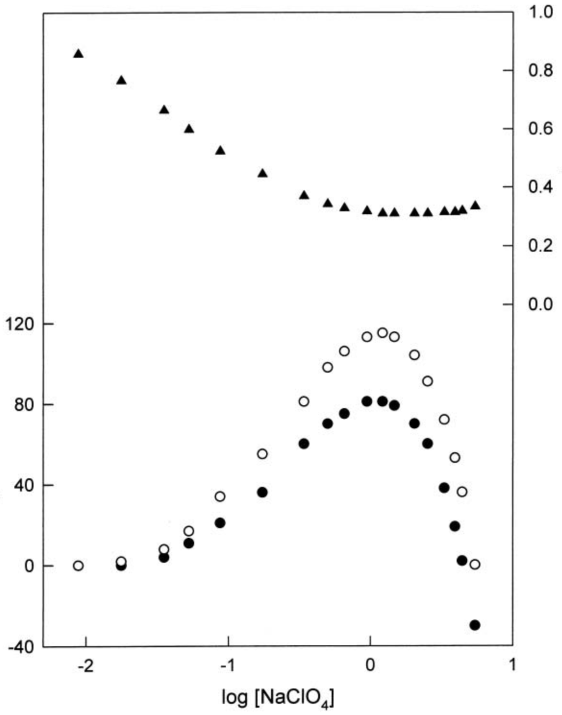

Figure 2. Influence of the $NaClO_4$ concentration on the peak current (▲) and the shift of the peak potential – both normalized with respect to the values recorded in 0.01 mol L^{-1} $HClO_4$. Europium concentration: 0.1 mmol L^{-1}, SW amplitude: 50 mV, scan increment: 2.1 mV, SW frequency: 20 (●) and 100 (○) s^{-1}.

In SW voltammetry, the peak current decrease (under fixed measuring conditions) is mainly a consequence of the decreased electrode rate constant.[32] In the system of interest, this can be presented in a qualitative but illustrative way if the backward SW current (i_b) is followed at an increasing salt concentration (Figure 3A). Under such conditions, the europium reoxidation signal gradually decreases and finally attains the sigmoidal form whereas its peak potential changes only slightly. At the same time, the corresponding forward signal becomes lower and obviously shifted in the negative direction (80 mV for the perchlorate concentration range 0–0.48 mol L^{-1}). The electrode rate constant, higher in dilute than in concentrated electrolyte solutions, points to the Frumkin effect,[33] *i.e.*, the influence of the salt concentration on the electrode kinetics through changes in the double layer structure.

In comparison with the peak height, its width ($\Delta E_{p/2}$) is less sensitive to the electrolyte concentration. In the range 0.01–0.1 mol L^{-1}, the half-peak width is virtually

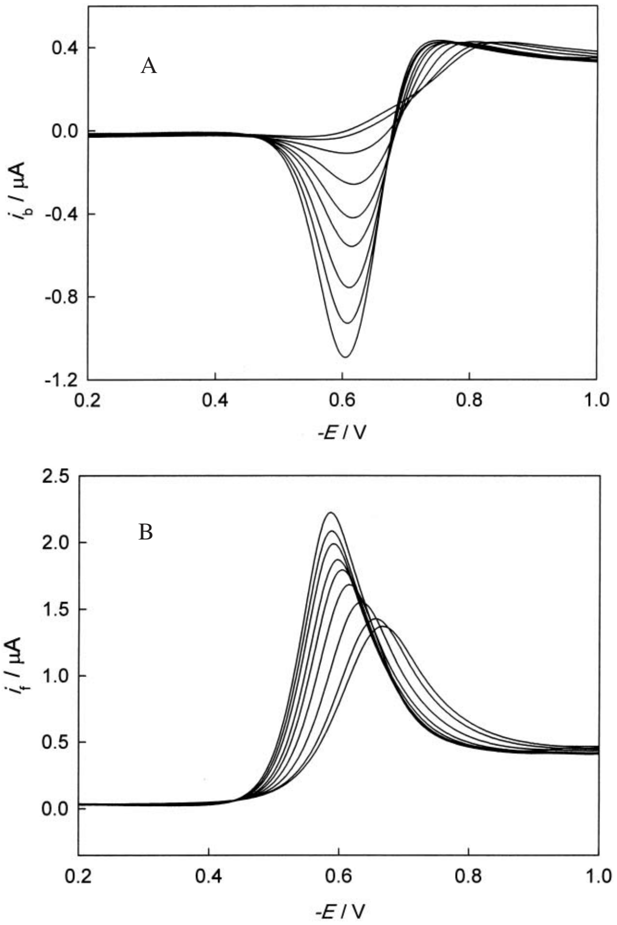

Figure 3. (A) Change of the SW backward current in dependence on the sodium perchlorate concentration (in the ascending order: 0, 0.008, 0.017, 0.034, 0.051, 0.084, 0.166, 0.325, 0.479 mol L^{-1}). (B) Corresponding SW forward currents, but in the descending order. Europium concentration: 0.5 mmol L^{-1}, SW frequency: 20 s^{-1}.

TABLE I. Characteristics of the maximum appearing on (ΔE_p) vs. log [electrolyte] plot[(a),(b)]

Electrolyte	$[Eu^{3+}]$	$(\Delta E_p)_{100}$	$(\Delta E_p)_{20}$	[electrolyte]
	mol L^{-1}	mV	mV	mol L^{-1}
$NaClO_4$	1×10^{-4}	115	81	1.2
	5×10^{-4}	105	83	1.2
NaCl	1×10^{-4}	124	87	1.1
NaBr	1×10^{-4}	52	11	0.5
$LiNO_3$	5×10^{-4}	77	49	0.7

[(a)] $\Delta E_p = E_p$(in 0.01 mol L^{-1} $HClO_4$) – E_p(in the solution of interest).
[(b)] $(\Delta E_p)_{100}$, $(\Delta E_p)_{20}$: number in the subscript denotes SW frequency.

constant, *i.e.*, similar or even somewhat lower than the theoretical value (124 mV) for a reversible one electron reduction process.[34] The signal becomes wider in more concentrated salt solutions, as follows from the positions of the forward and backward peaks in Figure 3. Dependence of $\Delta E_{p/2}$ on log [$NaClO_4$] is a sigmoidal curve, but values at the plateau depend on the applied conditions, again being higher at a higher frequency and lower europium concentration. The two mentioned dependencies (*i.e.*, of the peak current and half-peak width on log [$NaClO_4$]) are similar to the plots of the calculated signal characteristics *vs.* log κf (where $\kappa = k_a°/D_r^{\alpha/2}D_o^{(1-\alpha)/2}$) for slow electron transfer.[28] In other words, it seems as if the apparent standard rate constant is proportional to the electrolyte concentration, assuming that the changes of diffusion (D_r and D_o) and transfer coefficients (α) are of minor importance.

With an increasing sodium perchlorate concentration, the SW peak potential shifts negatively and then (at [$NaClO_4$] ≈ 1.2 mol L^{-1}) »returns« into the positive direction. If the salt concentration is higher than 4.5 mol L^{-1} and $f = 20$ s^{-1}, the peak position is more positive than in the reference solution (0.01 mol L^{-1} $HClO_4$). After passing through the maximum, the positive shift is continuous and can be observed in the whole accessible perchlorate concentration range, *i.e.*, until near saturation. The rate of the electrode process increases again in the most concentrated electrolyte solutions. Comparison of the results obtained at two metal concentrations (Table I) indicates that the maximum (negative) peak potential shift is virtually identical (82 mV) in both cases if SW frequency of 20 s^{-1} is applied. At $f = 100$ s^{-1}, however, these values differ significantly, being 115 mV at the lower and 104 mV at the higher europium concentration. This is a consequence of the previously mentioned influence of the total metal concentration on the response in the reference solution (0.01 mol L^{-1} $HClO_4$). At perchlorate concentrations higher than 0.1 mol L^{-1}, the difference $(E_p)_{100} - (E_p)_{20}$ does not depend on the level of the dissolved Eu^{3+} supposing that both potentials are given with respect to the applied Ag/AgCl electrode. In dc polarography the increase of perchlorate concentration shifts the signal in a similar way while the limiting current becomes higher (Figure 4). The corresponding dependence is given by $i_d/\mu A = 0.21 + 0.16\,[NaClO_4]^{1/2}$ for a europium concentration of 0.1 mmol L^{-1}. At the other level of dissolved metal (0.5 mmol L^{-1}), the linear dependence of i_d on $[NaClO_4]^{1/2}$ is maintained but the whole effect is less pronounced because of the lower slope (0.09) and higher intercept of the corresponding straight line.

In a stepwise dilution of 0.5 mmol L^{-1} Eu^{3+}, originally present in 0.01 mol L^{-1} $HClO_4$, with a highly concentrated solution of $NaClO_4$ (free from dissolved europium), the limiting current decreases significantly slower than expected from the change of the starting volume. After correction of the experimental values, *i.e.*, subtraction of the mentioned »salt contribution«, an acceptable agreement with »theoretical« currents was obtained.

Under otherwise identical conditions (constant timing parameters and electrode surface area), the wave current increases with increasing the diffusion coefficient and/or analyte concentration. As the viscosity becomes higher in more concentrated salt solutions,[35] no dramatically increased value of D_o is to be expected. Formation of some new species, such as differently hydrated europium(3+) ions, at a significant (relative) concentration is another possibility but most probably the origin of the observed effect should be found in double layer effects though additional studies are needed.

Reduction in Other Electrolytes

Similar SW experiments as described were also performed with NaCl, NaBr and $LiNO_3$. The results are presented in Table I together with the values for perchlorate solutions. In chloride media they are (qualitatively) of the same type as those already described – if the changes of peak height and potential with electrolyte concentration are followed. However, if perchlorate or chloride is substituted by nitrate or bromide, the maximum potential shift as a function of the salt concentration becomes sig-

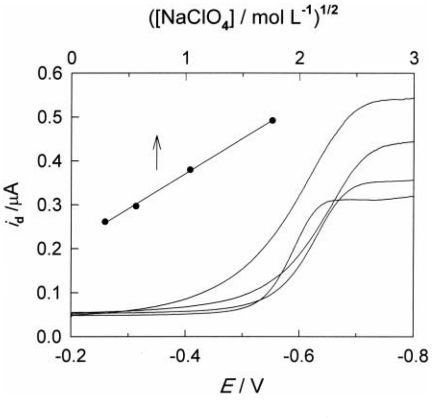

Figure 4. dc polarograms of 0.1 mol L^{-1} Eu^{3+} obtained at different levels of $NaClO_4$ (in the ascending order: 0.087, 0.320, 1.083, 3.090 mol L^{-1}) and a drop time of 0.5 s. The straight line gives the corresponding dependence of the limiting current on the square root of the salt concentration.

nificantly less pronounced. Additionally, in both cases its position appears at a lower salt concentration as if the effect of increasing electrolyte concentration were suppressed by some other phenomenon. According to the literature data,[25] the rate of the electrode process in chloride and perchlorate solutions should be similar ($k_a^\circ = 10^{-4}$ cm s^{-1}), significantly higher in bromide (and iodide) media ($k_a^\circ = 10^{-3}$ cm s^{-1}),[19, 22, 36] whereas solutions of $LiNO_3$ are interesting because of the inner sphere complexation. As pointed out by Kanno and Yokoyama,[5] the latter virtually prevents detection of »anomalous« hydration in nitrate media. Lis and Choppin,[4] however, reported that in solutions of $LiNO_3$, only a decrease of the hydration number at an increasing salt concentration could be observed by luminescence spectroscopy.

In perchlorate, chloride and bromide solutions, even at very high salt concentrations, the first coordination sphere of Eu^{3+} contains only water molecules.[3,37] In the nitrate medium, however, $EuNO_3^{2+}$ can also be formed. The corresponding stability constants for ionic strengths up to 4 mol L^{-1} ($\log \beta_1 = 0.2–1.2$) were published.[38] Assuming that no higher coordination species are present, the relative concentration of the »free« metal ion becomes less than 50 % if the ligand concentration exceeds 0.3 mol L^{-1}.

In more concentrated nitrate solutions (>0.5 mol L^{-1}), there is a pronounced increase of the basic current in square wave voltammetry and gradual disappearance of clearly defined limiting current in dc polarography. Although reduction of nitrate ions could be catalyzed by different lanthanides,[39] the mentioned effect is probably a consequence of hydrogen reduction, because a steep current increase at negative potentials is obvious even in acidic solutions of $LiNO_3$ that do not contain dissolved europium. It remains questionable if the phenomenon appears only as a »graphical« problem on the voltamograms (and polarograms) or perhaps the corresponding reaction and its products interfere with the process of interest. Anyway, in sampled-current dc polarography the increased concentration of lithium nitrate reduces the limiting current. Although the effect is not very pronounced, the wave height (after correction for the basic current) reaches only 86 % of the value recorded in 0.01 mol L^{-1} $HClO_4$ if the concentration of $LiNO_3$ is 4.9 mol L^{-1} (at t_d = 0.5 s and $[Eu^{3+}]$ = 0.5 mmol L^{-1}), demonstrating clearly that the electrode response is not governed by the same factors as in sodium perchlorate solutions.

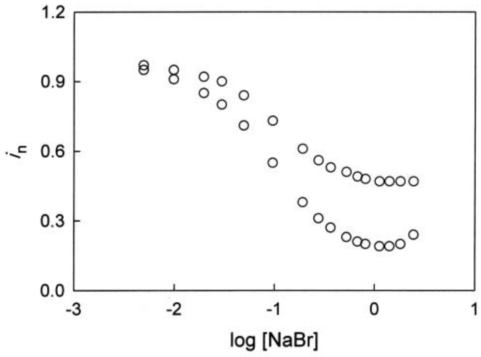

Figure 5. Dependence of the europium(3+) normalized SW peak height on bromide concentration at the frequency of 20 (upper curve) and 100 s^{-1} (lower curve). Metal concentration: 0.5 mmol L^{-1}, amplitude: 50 mV, scan increment: 2.1 mV.

In comparison with the other systems described, the SW results obtained in bromide media are characterized by more pronounced differences at the two SW frequencies applied. This especially holds for the peak currents. In the concentration range up to 2 mol L^{-1}, the backward current indicates more or less pronounced reoxidation if the frequency of 20 s^{-1} is applied. At 100 s^{-1}, however, the corresponding peak gradually disappears and a horizontal line is obtained instead. For all these reasons, the change of the normalized peak height as a function of the electrolyte concentration is (highly) frequency dependent (Figure 5) although the corresponding lines are placed close together in perchlorate solutions. Additionally, in bromide media the ratio of the absolute values, *i.e.*, $(i_p)_{100}/(i_p)_{20}$, gradually decreases and becomes only 0.75 at [NaBr] ≈ 1 mol L^{-1}. (In perchlorate solutions, the corresponding ratio increases up to 2.3.)

From these results, obtained in different electrolytes, it is not easy to find the role of water in the electrode processes of interest. Although at very high perchlorate concentrations, *i.e.*, a significantly reduced water activity, europium(3+) reduction becomes apparently faster, this could be a consequence of less pronounced double layer effects. In a classical paper of de Kreuk *et al.*,[40] there is a statement that europium ions do not lose their hydration shell before or during the reaction. In some other studies,[20.] however, a less hydrated product (in comparison with the reactant) was assumed, thus implying an important role of water molecules in the electrode process.

Reduction in Mixtures of Electrolytes

The best way of comparing the influence of individual electrolytes on the process of interest is to perform measurements in solutions of the same ionic strength (but different composition) because under such conditions variations of activity coefficients are not (very) pronounced. In order to confirm that gradual substitution of perchlorate by bromide ions at a constant ionic strength ($[NaClO_4]$ + [NaBr] = 1 mol L^{-1}) really changes the electrode response, a series of corresponding solutions was studied. Bromide concentrations up to 0.1 mol L^{-1} do not produce any obvious change of SW signals, but after that there is a pronounced peak potential shift in the positive direction, the difference between »extreme« solutions being 72 mV if the frequency of 20 s^{-1} is applied. At the same time, the peak current becomes 65 % higher than the value measured in the pure perchlorate medium of the same ionic strength (Figure 6). The higher rate of the electrode process is obvious from

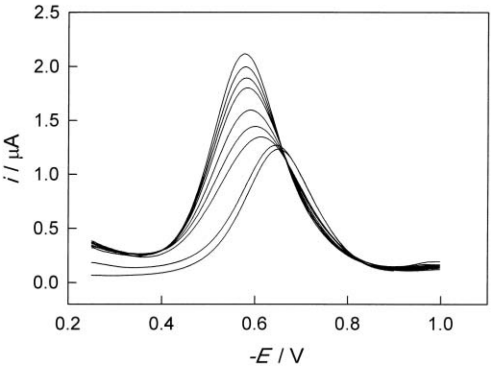

Figure 6. SW signals obtained in perchlorate–bromide mixtures at a constant ionic strength of 1 mol L^{-1}. Bromide concentrations (in the ascending order): 0, 0.039, 0.286, 0.375, 0.500, 0.625, 0.714, 0.833, 1 mol L^{-1}. Europium concentration: 0.5 mmol L^{-1}; frequency: 20 s^{-1}; amplitude: 50 mV; scan increment: 2.1 mV.

the shape of the forward and backward signals. In a pure perchlorate solution reverse current has the wave form (Figure 7A), whereas in the corresponding bromide medium it is a well developed reoxidation peak (Figure 7B).

If the change of the electrode response as a function of bromide concentration is also followed by sampled dc polarography (t_d = 1 s), the difference in the half-wave potential between the »extreme« solutions is only 45 mV whereas the difference between $E_{1/2}$ and E_p (in dependence on log [NaBr]) is a Z-shaped curve with the value of 32 mV at the plateau.

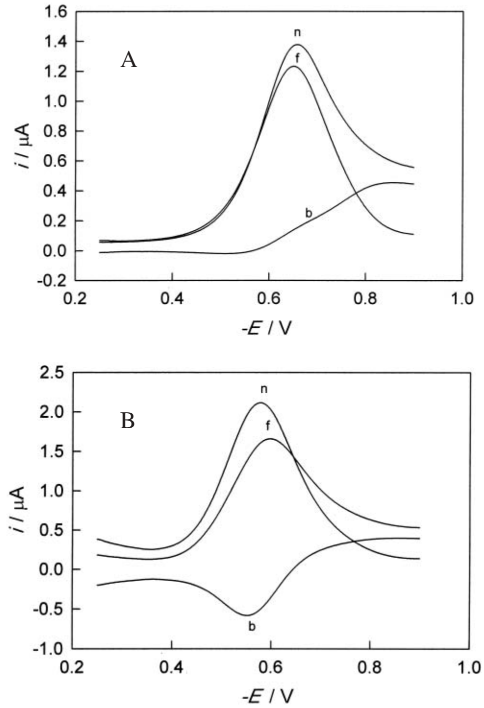

Figure 7. Forward (f), backward (b) and net (n) currents recorded in 1 mol L^{-1} of (A) $NaClO_4$ and (B) NaBr. Conditions correspond to Figure 6.

In an attempt to perform the same type of experiments but starting with a solution of pure NaBr and substituting it gradually with NaI (at a constant ionic strength of 1 mol L^{-1}) only dc measurements could be performed in a satisfactory way because SW signals were highly affected by the basic current. The results obtained at t_d = 0.5 s indicate that (during »transition« from 1 mol L^{-1} of NaBr to 1 mol L^{-1} of NaI) the half wave potential is shifted in the positive direction (20 mV) whereas the apparent αn value becomes 1 again.

If the above type of study is performed with a pair of salts having the same anion but different cations (without pronounced surface activity), *i.e.*, $NaClO_4$ and $Mg(ClO_4)_2$, the change of their individual concentrations, at a constant ionic strength of 1 mol L^{-1}, does not influence the characteristics of the europium(3+) reduction signal.

Concluding Remarks

The aim of the present article was to describe the voltammetric behavior of Eu^{3+} in a wide concentration range of different salts because no such results could be found in the literature and SWV had never been applied in studies of europium(3+) reduction. Further, it was interesting to see if the published data obtained by other methods, according to which europium hydration seems to increase with increasing perchlorate or (perhaps) chloride concentrations while the opposite effect appears in nitrate medium, could be confirmed.

In perchlorate and chloride solutions, in which inner sphere complexation and anion adsorption are not (very) pronounced, the peak potential shifts negatively with an increasing salt concentration until nearly 1.2 mol L^{-1} and then returns in the positive direction. Under otherwise identical conditions, the maximum on the corresponding plot is significantly less pronounced and translated towards lower concentrations if nitrate is used instead. Taking into account that the inner sphere complexation can be treated as a substitution of water molecules with ligand ions, the latter seems reasonable. The question arises whether a plot of the peak potential shift in dependence on the salt concentration could be generally used as a diagnostic criterion. In other words, whether the height and position of the corresponding maximum, obtained at a not too low SW frequency, is an indication of the »situation« in the solution and/or at the electrode/electrolyte interface. It would be interesting to perform similar measurements with europium ions and other highly soluble salts of different acids whose anions are »inert«, surface-active or can form inner sphere complexes. Such results could perhaps give the answer to whether the pronounced maximum appearing at the electrolyte concentration of about 1 mol L^{-1} (followed by a steep shift in the positive direction) can really be obtained only in systems characterized by a reduced luminescence life-time, previously interpreted as an indication of the increased hydration number at decreased water activity. In a similar way, lower and translated maxima could be indications of the inner sphere complexation or reduction according to the bridge mechanism. The two latter cases can be distinguished if the peak height decrease resulting from an increasing electrolyte concentration is followed at two frequencies, because it seems that two significantly different curves can be obtained only for reduction *via* the adsorbed anion. In addition, following the wave height in dc polarography, *i.e.*, detection of its increase with increasing the electrolyte concentration, could also help in some systems.

To distinguish between the influence of changes in the aqueous phase and at the mercury/solution interface, it would be necessary to apply some other electrochemical techniques. Such results, along with the corresponding model calculations, could confirm or reject the existence of europium(3+) »anomalous« hydration and help obtain a (more) quantitative description of the reduction process, including recognition of all the factors that influence the electrode response.

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SAŽETAK

Elekrokemijska redukcija europija(3+) pri rastućim koncentracijama različitih soli. I. dio – Voltametrijska mjerenja

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Pod utjecajem spektroskopskih rezultata, koji kao da ukazuju na porast hidratacijskoga broja pri smanjenom aktivitetu vode u perkloratnim i (nekim) kloridnim otopinama, ponovno je ispitana elektrokemijska redukcija europija(3+) u različitim elektrolitima. Spomenuti anioni zaista slično utječu na elektrodni odziv kad se pomak potencijala i smanjenje struje vrha u pravokutnovalnoj voltametriji prate u ovisnosti o koncentraciji elektrolita. U nitratnome, bromidnome i jodidnome mediju rezultati se znatno razlikuju zbog stvaranja europijevih unutrašnjih kompleksa ili promjene elektrodne kinetike pod utjecajem adsorbiranih aniona. Ostaje upitno mogu li se odgovarajući rezultati (zajedno s onima iz dc polarografije) rabiti za dijagnostičke svrhe kad je riječ o europiju(3+) u otopinama manje poznatih elektrolita, tj. za razlikovanje procesa koji uključuju »inertne«, površinski aktivne i kompleksirajuće anione.