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ORIGINAL PAPER

Silver electrowinning from silver(I)–calixarene complexes by two-phase electrolysis

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Abstract Results are reported, providing the basis for an elegant new process for metal recovery from acidic solutions, by integrating solvent extraction (SX) and electrowinning (EW) in a single process, rather than operating them separately, as in conventional SX–EW processes. Calixarene-tetramide and its thio-analogue were used for the extraction of silver(I) ions from aqueous phases into dichloromethane, both compounds achieving extraction efficiencies >90%. The effects were determined of extractant and silver(I) concentrations, aqueous phase pH, and the presence of sodium ions, on the distribution of Ag(I) between aqueous and organic phases. Due to the impossibility of stripping the extracted metal conventionally, electro-reductive stripping of silver(I) from the loaded organic phase was carried out in the calixarene/nitric acid two-phase system. The effects were also investigated of current density or electrode potential on silver deposition current efficiencies and cell voltages. Based on experimental data, a new process for silver(I) removal from very dilute solutions was proposed that showed high percentage extractions of silver(I) from the aqueous phase, coupled to direct EW of silver from the calixarene complex in the loaded organic phase, regenerating the extractant for recycle. Current efficiencies in the range from 60% to 90% and cell voltages <3.5 V were achieved simultaneously in this process.

Keywords Calixarene · Electrowinning · Electroreductive stripping · Silver recovery · Solvent extraction

Notations

A_a	Anode area (cm^2)
A_c	Cathode area (cm^2)
C_b	Concentration of silver(I) in the bulk electrolyte (mol dm^{-3})
C_L	Relative concentration of extractant (mol/mol Ag^I)
C_w	Concentration of silver(I) in the aqueous phase (mol dm^{-3})
d	Electrode diameter (mm)
D	Diffusion coefficient (cm^2 s^{-1})
$Dep_{i.\mathrm{Ag}}$	Mass of deposited silver at ith cycle (mg)
E	Electrode potential (V)
E_i	Mass of silver in the organic phase at ith cycle (mg)
F	Faraday constant (C mol^{-1})
F_i	Mass of silver(I) in the feeding solution at ith cycle (mg)
j	Current density (mA cm^{-2})
j_L	Limiting current density (mA cm^{-2})
j_p	Peak current density (mA cm^{-2})
M	Molar mass of silver (g mol^{-1})
R_i	Mass of residual silver(I) in raffinate at ith cycle (mg)
t	Time (s)
U	Cell voltage (V)
v	Scan rate (mV s^{-1})

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w_{Ag}	Specific electrical energy consumption (kWh (tonne)$^{-1}$)
z	Electron stoichiometry/charge number of reaction
Φ^{e}_{Ag}	Current efficiency
AEP	Additional extraction percentage
EP	Extraction percentage
EWD	Electrowinning degree

1 Introduction

Numerous processes for metal recovery from various effluents have been developed since the 1960s. Solvent extraction (SE)/stripping processes (SX), followed by electrowinning (EW) of metal from the loaded stripping solution, have frequently been considered as a method for selective removal and recovery of particular metals from aqueous streams. The aim was to define appropriate extractants capable of complexing the targeted metal ions selectively and quantitatively from sources containing initially low concentrations of those ions in rinse and wastewaters. Applications have included noble metals, because of their high price and toxicity, but also heavy metals, as harmful pollutants for surface and groundwaters [1].

Calixarenes and their derivatives have attracted considerable attention as novel extractants, able to recognize and discriminate metal ions, making them suitable as specific receptors [2–4]. In these studies, silver(I) has been investigated more frequently than the other metals [5–7], including palladium and platinum and heavy metals alone or in mixtures with different noble metals [5, 7]. It was found that alkali and alkaline earth metals would be co-extracted readily with most calixarenes [2, 4, 7–10].

However, most studies of calixarenes as extractants hitherto were fundamental or were performed for analytical purposes; those few publications about stripping of noble metals by complexing them with calixarenes, reported <40% stripping of the extracted metal [9, 10]. The process for which results are reported below, circumvented such difficulties of stripping silver(I) back to an aqueous phase conventionally, by EW of the complexed metal directly from the loaded organic phase, regenerating the extractant. The application of two-phase electrolysis in the electrochemical synthesis of organic substances has been shown as an attractive method having several technological advantages [11, 12]. Some calixarenes have been studied not only for the electrochemical determination of barium(II) [13], calcium(II) [14] but also silver(I) [15] and other metal species [16]; this encouraged the authors to investigate the electrochemical stripping of silver(I) bonded to calixarene in an organic phase.

Though they have good extraction abilities and acceptable costs, the solubility's of these extractants in commercial organic diluents are low. Calixarenes are readily soluble in chlorinated-organic solvents, such as dichloromethane, chloroform, nitrobenzene, acetonitrile and other, mainly toxic, solvents. This lack of acceptable solvents is a significant barrier to industrial applications of calixarenes, so investigations have to be oriented towards substitution of these hazardous solvents with some other less toxic and environmentally more acceptable compounds [17]. On the other hand, solvents like dichloromethane and chloroform could be very useful for some particular extraction processes, as they have low viscosity and considerably higher density than water, properties ensuring fast and efficient phase separation.

In spite of its disadvantages, dichloromethane is known as being electrochemically stable, with a wide potential window. A few preliminary voltammetric experiments, made by the authors, with silver(I)–calixarene complexes were promising, indicating that it should be possible to reduce silver(I)–calixarene complexes in the loaded organic phase. However, it is discouraging that calixarene amides can easily be electrochemically oxidized to a calixquinone form, losing their primary properties [18, 19].

This paper reports a new method for silver recovery from dilute acidic aqueous solutions, using SX followed by the electrochemical stripping of the extracted silver(I)–calixarene complexes by their cathodic reduction to elemental silver directly from the loaded organic phase in the two-phase system, with the aim of enabling the recycle of released calixarene for further extraction.

2 Experimental

2.1 Chemicals and solutions

Two calix[4]arene amide derivatives were employed as extractants for silver(I) in the SX/EW process:

Calix[4]arene-tetramide (5,11,17,23-tetra-*t*-butyl-25,26,27,28-tetrakis(*N*,*N*-diethylaminocarbonil)methoxocalix[4]arene—LBC); and its thio-form: calix[4]arene-thiotetramide: 5,11,17,23-tetra-*t*-butyl-25,26,27,28-tetrakis(*N*,*N*-diethylaminothiocarbonil)methoxocalix[4]arene—THIO. Structural formulae of these calixarenes are shown in Fig. 1.

LBC and THIO were both synthesized in the Laboratory of Organic Chemistry of HEVs Sion, Switzerland, starting from *p*-*t*-butylcalix[4]arene, kindly provided by the CAL-X Group from Saxon, Switzerland. The calixarenes were dissolved at their (ambient temperature) solubility limit of 10^{-2} mol dm^{-3} in dichloromethane, previously contacted

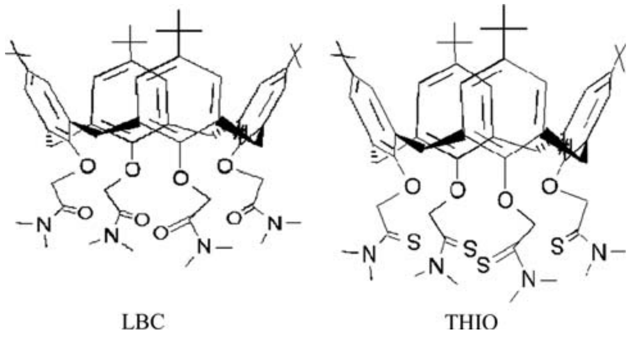

Fig. 1 Structural formulae of the two calixarenes used

with 0.1 mol dm^{-3} aqueous nitric acid solution to increase its conductivity.

The transfer of 10^{-2} mol dm^{-3} silver(I) from an acidic aqueous solution to the organic phase by calixarenes was used as a model system in this study. The aqueous solution of silver(I) was prepared using silver(I) nitrate solution (0.1 mol dm^{-3}), supplied by Fluka. Depending on the experiment, these starting solutions were further diluted by dichloromethane—the organic phase (O), or by 0.1 mol dm^{-3} nitric acid solution–the aqueous phase (A). In those experiments in which the influence of pH was studied, the concentration of nitric acid was varied from 0.1 mol dm^{-3} to zero.

2.2 Solvent extraction experiments

Solvent extraction of silver(I) from nitric acid aqueous solution was carried out by shaking equal volumes of the chosen extractant and silver(I) nitrate solution (O:A = 1:1), for 5 min in a separating funnel and left for 1 h for phase separation. Then samples of the aqueous phase were taken and the concentration of residual silver(I) was determined by atomic absorption spectrophotometry (Shimadzu AAS 665-X). The concentration of silver(I) transferred to the organic phase was calculated from the mass balance. A series of distribution experiments were performed, varying the concentration of extractants, changing pH, adding sodium ions, with the aim of evaluating the extraction percentage (EP), the process stoichiometry, the distribution coefficient and the other data relevant for the SE process, such as the loading capacity, selectivity, stripping conditions etc., have also been evaluated and will be published [20].

The electrochemical experiments were performed in a three electrode glass cell, equipped with a magnetic stirrer. A platinum wire spiral ($A_a = 4$ cm^2) served as the anode in all experiments. For the cyclic voltammetry and chronoamperometry measurements, either a platinum wire ($d = 1$ mm, 3 mm length) or a titanium rod ($d = 2.2$ mm) was used as the cathode. Only the length indicated in the brackets and the frontal part of platinum were in contact with the electrolyte, the rest of the wire being insulated by a plastic coating insoluble in dichloromethane. In case of the titanium rod, only the frontal surface served as the cathode, the rest being insulated with the same plastic coating. Either a platinum plate ($A_c = 2$ cm^2) or titanium plate ($A_c = 4$ cm^2) electrode, soldered to a copper wire conductor sealed in a glass tube, was used as the cathode in the EW experiments. A silver wire, positioned close to the cathode, served as a pseudo-reference electrode. As depicted in Fig. 2, the anode was immersed in the aqueous phase (raffinate), while the cathode was placed into the organic phase loaded with silver(I). The inter-electrode distance was approximately 2 cm.

Placing the anode in the aqueous phase should have prevented exposure of the extractant to oxidising conditions, thus preventing its anodic destruction; anodic oxygen evolution occurred in the aqueous phase, while silver(I) reduction occurred in the organic phase. Prior to immersion of the titanium electrode in the cell, the thickness of the oxide layer on its surface was minimised by sand blasting it for a few seconds and then washed in an ultrasonic bath with a mixture of 2-propanol and distilled water. Platinum electrodes were only washed in the ultrasonic bath.

A computer controlled potentiostat/galvanostat (Autolab PGstat 30, Eco Chemie B.V.) was used.

2.3 Experimental procedure and sample analysis

Prior to the electrochemical experiments, SX of silver(I) was carried out using 0.01 mol dm^{-3} starting solutions, as

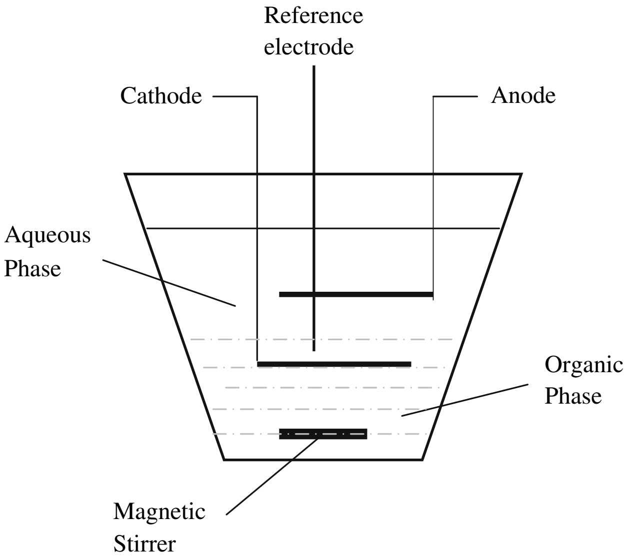

Fig. 2 Schematic presentation of three electrode cell

described previously. Based on the process stoichiometry, adequate volumes of the chosen extractant and silver(I) nitrate solution were shaken in a separating funnel, left for phase separation and then introduced into the cell, in which the lower organic layer loaded with silver(I) was used as a catholyte and the upper aqueous layer served as anolyte. The ionic conductivity of the acid-free dichloromethane is 10^{-5} S m^{-1} [11], whereas that of wetted dichloromethane is almost one order of magnitude greater and would have been increased further by dissolving the silver(I) complexed with calixarene [5]. To decrease ohmic potential losses, 0.01 mol dm^{-3} tetra-butyl-ammonium perchlorate (TBAP) was added as a supporting electrolyte.

Experiments were performed at ambient temperature that varied from 19 to 21 °C in the air-conditioned laboratory.

3 Results

3.1 Solvent extraction and process stoichiometry

To obtain information on the extent of silver(I) extraction, process stoichiometry and the distribution equilibrium of the extractants, distribution experiments were carried out, keeping the concentration of silver(I) constant at 10^{-3} mol dm^{-3} and varying the concentration of extractants in the range from 1×10^{-4} to 2×10^{-3} mol dm^{-3}, corresponding to extractant to metal molar concentration ratios (C_L:$C_{Ag(I)}$) from 0.1 to 2.

Figure 3 shows the effect of changing that molar ratio on the silver(I) concentration in the aqueous phase; the experiments were duplicated to determine their reproducibility.

It is clear that both LBC and THIO were efficient extractants for silver(I), achieving EPs >80% with LBC, and >99.9% with THIO, for C_L:$C_{Ag(I)}$ of unity. Higher EPs were achieved by adding LBC in excess; e.g. >90% of silver(I) was extracted with C_L:$C_{Ag(I)}$ of 1.4. THIO extracted silver(I) almost quantitatively just adding an amount slightly exceeding the value of 0.5 moles per mole of silver(I).

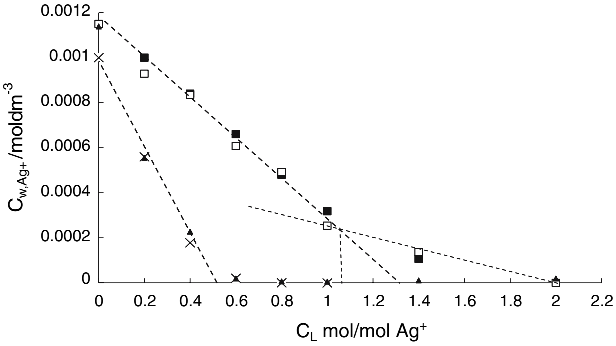

Fig. 3 Effect of LBC and THIO extractant to silver(I) molar ratio on silver(I) extraction. Initial concentration of silver(I) = 10^{-3} mol dm^{-3}; O:A = 1:1; ▲, ×(duplicate)—THIO; ■, □ (duplicate)—LBC

From the experimental data in Fig. 3, it is also evident that the stoichiometry of silver(I) complexation with LBC and THIO differed. From the points of the linear parts intersection on the graphs (dashed lines) and their projection on the *x*-axis [5], the following reaction stoichiometry for silver(I) complexation by THIO was suggested:

$$2Ag^+_w + 2NO^-_{3,w} + L_o \leftrightarrow [(Ag^+)_2L](NO^-_3)_{2,o} \qquad (1)$$

For LBC, the gradient of the line in Fig. 3 was close to unity, indicating a 1:1 molar ratio of silver(I) and calixarene, suggesting the following reaction occurred:

$$Ag^+_w + NO^-_{3,w} + L_o \leftrightarrow [Ag^+L]NO_{3,o} \qquad (2)$$

Here, L represents the calixarene as extractant and the subscripts w and o refer to the aqueous and organic phases, respectively. Other useful data about the SX are summarized in Table 1.

Though both extractants had very high EPs for silver(I), the loading capacity of THIO was twice that of LBC, THIO was equally effective in acid and neutral solutions and was not sensitive to Na^+ ions, making it the preferred extractant for selective removal of silver(I) from sources containing such ions.

3.2 Cyclic voltammetry and chronoamperomety

Figure 4a shows typical voltammograms for reduction of silver(I) complexed with THIO in dichloromethane, recorded in this case by using a titanium rod electrode (2.2 mm diameter). Two reduction current peaks were evident at potential scan rates ≤50 mV s^{-1}; that ca. –750 mV (vs. Ag^I/Ag) (at 20 mV s^{-1}) was well defined, while the peak at ca. –1 V (vs. Ag^I/Ag) was smaller, poorly defined and disappeared at higher scan rates. Reduction current peaks shifted to more negative potentials with increasing scan rate, as expected for an irreversible reduction process, such as silver phase formation. The linearity of the cathodic peak currents plotted against the square root of the scan potential rate in Fig. 4b implies that reduction of the silver(I) complex was diffusion controlled. Indeed, the non-zero intercept by extrapolation to zero scan rate suggested a second, kinetically controlled reaction. According to the literature [21–23], there are two possibilities that will require further investigation:

- Reduction of nitrate in the organic phase, that occurs electro-catalytically on platinum electrodes [21, 22];

Table 1 Solvent extraction of silver(I)—working conditions and results

Property/extractant	THIO	LBC
Ratio of O:A phase volumes	1:1	1:1
Amount of calixarene to achieve the highest EP	0.6 mol/1 mol Ag^I	1.4–1.5 mol/1 mol Ag^I
EP of silver(I)	>99%	95–97%
Colour of the complex	Brown	Colourless
Transparency	Slightly turbid	Transparent
Influence of pH in the range 1–6	No effect	Higher the pH, the lower EP
Influence of Na^+ concentration on EP of silver(I)	No effect in the range of 0.001–0.2 mol dm^{-3}	EP decreased more than 10-fold in the same range

Note: Initial concentration of Ag^I was 10^{-3} mol dm^{-3}

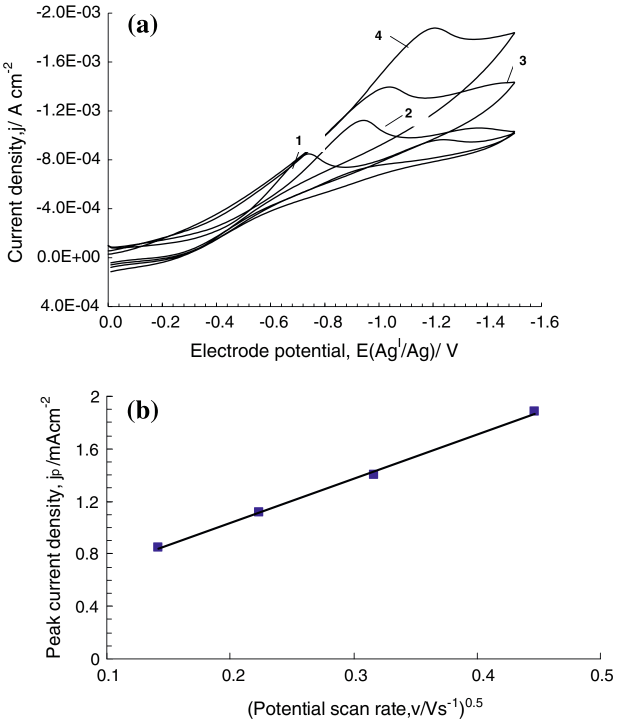

Fig. 4 (**a**) Cyclic voltammograms of 0.01 mol dm^{-3} Ag^I-THIO complex in dichloromethane on titanium electrode at different scan rates: 1–20 mV s^{-1}; 2–50 mV s^{-1}; 3–100 mV s^{-1}; 4–200 mV s^{-1} (**b**) Plot of current peaks at less negative potentials against square root of potential scan rate

- Dehalogenation of dichloromethane on freshly deposited silver [23], at potentials <–1.5 V (SCE).

The same electrodes and solutions from the voltammetric experiments were used to obtain chronoamperograms, for which the cathode potential was –750 mV (vs. Ag^I/Ag), corresponding to the less negative current peak at 20 mV s^{-1} in the voltammograms (Fig. 4a). Figure 5 shows that for Ag^I solutions of both extractant, linear plots of current density against time$^{-0.5}$, were obtained in accordance with the Cottrell equation:

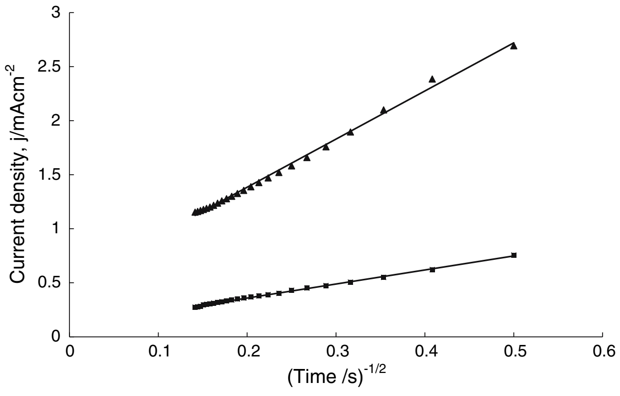

Fig. 5 Linearization of chronoamperometric data according to the Cottrell equation: ▲, Ag–THIO complex; ■, Ag-LBC complex: Initial concentration of silver(I) in the aqueous phase before the extraction—0.01 mol dm^{-3}; Cathode, platinum wire

$$j_L = \frac{zFD^{1/2}A_c C_b}{(\pi t)^{1/2}}. \tag{3}$$

While again this suggests a diffusion controlled process was operative, the finite current intercept at infinite time implies a kinetically controlled process in parallel, as mentioned in the discussion of the voltammetric experiments.

From a phenomenological point of view, the process of silver(I) SX/EW in a two-phase system includes three major steps [24]:

i. Mass transfer of Ag^I from the aqueous to the organic phase; transport of the silver(I)–calixarene complex from the bulk organic phase to the cathode; decomposition of the complex at the cathode; silver deposition; transfer of the reaction products (nitrate ions and released calixarene molecules) away from the cathode to the bulk;
ii. In the aqueous phase, mass transport of protons, generated by anodic water oxidation, to the liquid/liquid interface;

iii. Ion discharge reaction at the interface that comprises transfer of NO_3^- ions from the bulk to the interface to fulfil the charge balance with H^+ ions and mass transfer of nitric ions in the aqueous phase away from the interface.

The following stoichiometric reactions in the overall process are supposed:

At the anode, water oxidation generated oxygen and protons:

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \quad (4)$$

At the cathode, for the Ag-THIO complex:

$$Ag_2L(NO_3)_2 + 2e^- \rightarrow 2Ag + L + 2NO_3^- \quad (5a)$$

and similarly, for Ag-LBC complex:

$$AgLNO_3 + e^- \rightarrow Ag + L + NO_3^- \quad (5b)$$

3.3 Electrowinning of silver in two-phase system

During EW experiments, the organic phase was stirred gently at 100 rpm, to decrease concentration polarization, while minimising disruption of the liquid/liquid interface. The aqueous phase was sampled and analysed by means of atomic absorption spectrophotometry (AAS) to determine the actual concentration of silver(I) in the organic phase initially after extraction and after EW. Electrodeposited silver was dissolved in a known volume of a nitric acid solution and analysed. The results obtained enabled a mass balance to be made in both the SX and EW stages.

Electrowinning experiments were carried out in both galvanostatic (at different current densities) and potentiostatic modes (at different cathode potentials), while monitoring the cell voltage and either currents (potentiostatic) or cathode potentials (galvanostatic). These data, together with the distribution data of silver(I) between phases, enabled the overall current efficiencies (Φ^e_{Ag}) for electrodeposition of silver to be calculated, for the range of conditions summarised in Table 2.

Current efficiencies of 60–90% imply that some of the charge passed was used in side reactions such as nitrate and/or dichloromethane reduction, as mentioned in the discussion of the voltammetric results. These data demonstrated the feasibility of efficient electrode deposition of silver directly from the organic phase, though the deposit was powdery and was poorly adherent to the cathode. This was anticipated in the case of the Ti cathode, on which the presence of an oxide would have precluded any alloy formation. Silver is well known to produce dendritic depositions even from aqueous solutions, especially under transport control.

Table 2 Conditions and results for two-phase electrowinning of silver

Extractant	THIO	LBC
Cathode	Pt, Ti	Pt, Ti
Anode	Pt	Pt
Current density (mA cm^{-2})	0.5–2	0.25–2
Stirring	Magnetic	Magnetic
Deposit structure	Powdered	Powdered
Deposit colour	Black	Black
Deposit adhesion	Poor	Poor
Recycling of organics	Very good	Very good
Batch electrowinning conversion of Ag^I	50–80%	60–90%
Current efficiency, Φ^e_{Ag}	60–90%	60–80%
Additional extraction percentage	20–30%	≈30%

Note: Initial concentration of Ag^I, before the extraction, was 10^{-2} mol dm^{-3}

Table 2 also specifies, for both extractants, high values of the additional extraction percentage (AEP), a measure of how much silver(I) was additionally transferred from the aqueous to the organic phase, due to EW disturbing the liquid/liquid equilibrium, and causing further transfer of silver(I) species from the aqueous to the organic phase. The AEP depends strongly on the deposition rate, which depends on the applied current density or applied potential, as well as on the process time.

Most importantly, neither extractants lost their extraction abilities during the EW process; neither chemical nor electrochemical changes of the organic phase were detected during the experiments, so that it is possible to recycle the recovered extractant back to the extraction stage during the EW silver from the Ag(I)–calixarene complex. Five cycles were conducted consecutively with both extractants, where each cycle implies one SX and one EW stage. Results for the first and fifth cycles are presented in Fig. 6.

In the first cycle, silver(I) from the feed solution in contact with fresh extractant, was transferred into the organic phase, with a very high EP in the extraction stage that was increased slightly to >99.6% due to the AEP during EW.

In the EW stage, the loaded organic phase was depleted of silver(I) by almost 81%. Spent organic phase, containing residual silver(I)–calixarene complex, was mixed with fresh feed solution in the second cycle. The extent of extraction achieved in the second cycle was lower than that in the first cycle, due to the residual amount of complexed silver(I) not removed in the previous EW stage, so partially decreasing the extractant capacity. Thus, the deposited EP in each cycle will depend on the working conditions (working current density, or potential) in the EW stage of

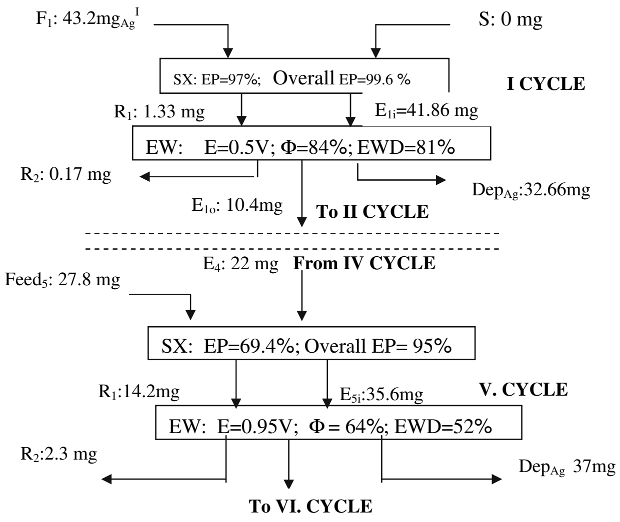

Fig. 6 Distribution of silver(I) in solvent extraction followed by two-phase electrolysis of silver(I) from the loaded organic phase: THIO is used as an extractant; potentiostatic mode of operation $E_{n,i}$, $E_{n,o}$—mass of silver(I) in the organic phase before and after electrowinning, in nth cycle, respectively; R_1, R_2—mass of silver(I) in the raffinate before and after electrowinning, respectively

that cycle. In any case, a certain amount of silver(I) will be re-circulating in the organic phase through the process, as in conventional SE–EW processes. Due to the AEP effect, the overall EP (defined as a sum of EP and AEP) did not change significantly and remained close to that achieved in the first cycle. This means that the EP in a certain cycle depends strongly on the EW conversion in the previous cycle, while the loading capacity of the extractant remains almost constant and independent of the number of cycles.

The same experiments as described above were also carried out with LBC, which produced similar results, listed in Table 2, confirming that it was possible to successfully reuse this extractant also.

In all experiments, the cell voltage (U) did not exceed 3.5 V, so that specific electrical energy consumptions (w_{Ag}) of silver recovery, defined by:

$$w_{\mathrm{Ag}} = \frac{FU}{3.6\Phi^{\mathrm{e}}_{\mathrm{Ag}} M_{\mathrm{Ag}}}\ \mathrm{kWh}\ (\mathrm{tonne\ Ag})^{-1} \tag{6}$$

would be in the range of 850–1,450 kWh (tonne Ag)$^{-1}$. However, this could be decreased by optimising current efficiencies, and by decreasing the inter-electrode gap and adding more (electro-inactive) supporting electrolyte to increase the solution conductivity and so decrease the ohmic potential drop contribution to the cell voltage. At this stage of establishing the process, it is too early to discuss process optimisation, but the specific electrical energy consumptions achieved can be considered satisfactory, when compared to those values of ≈800 kWh (tonne Ag)$^{-1}$ for EW silver under industrial conditions.

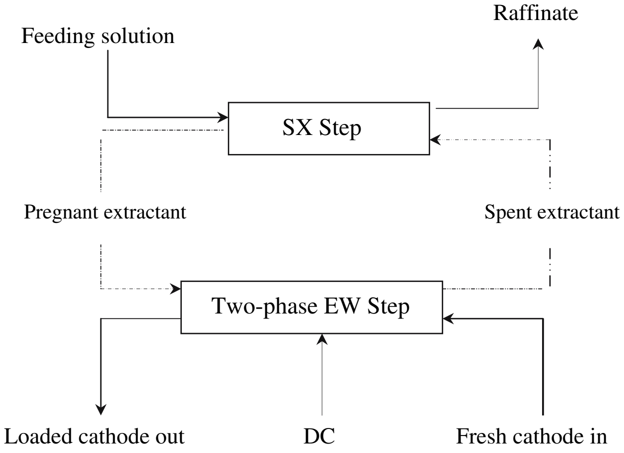

Fig. 7 Block diagram of the solvent extraction/two-phase electrowinning process

3.4 Proposed process for two-phase electrowinning of silver

Conventional extraction/EW processes involve three stages: extraction, stripping and EW. In the proposed process, the stripping and the EW steps are coupled, as shown schematically in Fig. 7, so that the proposed process consisted of only two steps. Ionic species from the aqueous feed solution entering the SX step, are extracted by the organic phase. Depleted aqueous phase—raffinate leaves the system as an off-stream. Loaded organic phase enters the EW step to be depleted in metal. After releasing metal in the EW stage, the spent extractant is recycled back to the extraction step. The cathode loaded with deposited metal, is periodically harvested from the cell for further processed. A fresh cathode would be introduced in the cell, replacing that loaded with deposited metal.

In spite of the process described being far from application, several benefits could arise from the EW of metal complexed by calixarene from the loaded organic phase: the process is simpler, so that capital, operating and maintenance costs should be lower. Thanks to the AEP, it would be possible to run a SX/EW process continuously in one unit, such as the mixer/settler design, as illustrated schematically in Fig. 8. In this mode, the aqueous phase passes through the unit in a single pass, while the extractant forms a closed circuit.

4 Conclusions

Both THIO and LBC were demonstrated to be effective extractants for silver(I) from aqueous solutions into dichloromethane. Having EPs >99% in case of THIO, it is possible to remove silver(I) selectively with this calixarene

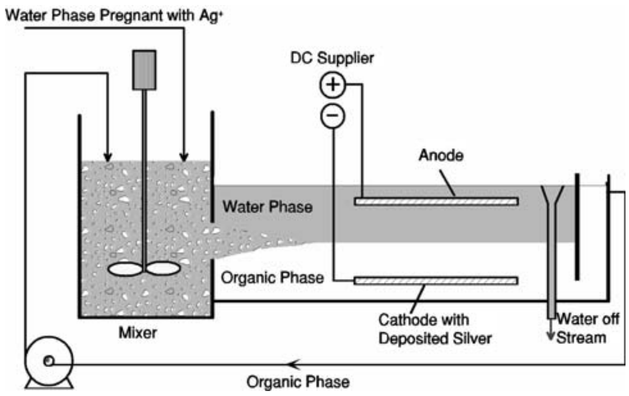

Fig. 8 Schematic of electrode configuration and phases flowing in combined mixer-settler extractor and electrochemical reactor

from acid or neutral solutions containing alkali metals, achieving concentrations in the raffinate of $<10^{-7}$ mol dm^{-3}. THIO also appears to be better than LBC, having twice the loading capacity, higher EPs, independently of the pH of the aqueous phase. Also, THIO did not complex sodium ions, while LBC had a high affinity for Na^+, often present in solutions containing silver(I).

The EW of silver directly from the organic phase, keeping the anode in the aqueous phase appears to be a novel and effective means of metal recovery, achieving current efficiencies of 60–90% and EW conversions with an acceptably low cell voltages, leading to specific electrical energy consumptions of 850–1,450 kW h (tonne Ag)$^{-1}$, though at current densities of only 2 mA cm^{-2}, limited by the process rate and low concentration of silver(I)–calixarene complex. Both calixarenes remained unchanged during the EW process, in principle, enabling there re-used indefinitely. Depending on the silver(I) conversion during EW, a certain amount of complexed silver(I) will be captured and circulate with the organic phase throughout the process, as in conventional SX-EW processes.

These early results are the first, encouraging step in establishing the new process for metal recovery from wastewaters by means of the two-phase electrochemical reduction of a metal–calixarene complex formed in the SE process. The EW of silver(I), complexed by calixarenes, was used as a model reaction system in these investigations; but one can assume that other metal complexes, having similar characteristics, should behave similarly, widening the process applicability and opening new frontiers in electrochemical technology and electrochemical engineering.

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References

1. Stankovic V (2007) Chem Biochem Eng Q 21(1):33
2. Gutsche CD (1989) Calixarenes. Royal Society of Chemistry, Cambridge
3. Ohto K, Murakami E, Shinohara T, Shiratsuhi K, Inoue K, Iwasaki M (1997) Anal Chim Acta 341:275
4. Danil de Namur AF, Zapata-Ormachea ML, Hutcherson RG (1998) J Phys Chem B 102:7839
5. Danil de Namur AF, Goitia MT, Casal AR, Villanueva-Salas JA (2001) Phys Chem Chem Phys 3:5242
6. Ouchi M, Shibutami Y, Yakobe K, Shono T, Shintani H, Yoneda A, Hakushi T Weber E (1999) Bioorg Med Chem 7:1123
7. Yordanov AT, Roundhill DM, Mague JT (1995) Inorg Chim Acta 240:441
8. Regnouf-de-Vains JR, Dalbavie JO, Lamartine R, Fenet B (2001) Tetrahedron Lett 42:2681
9. Ohto K, Jamaga H, Murakami E, Inoue K (1997) Talanta 44:1123
10. Yordanov AT, Roundhill DM (1998) Coordination Chem Rev 170:93
11. Hoh YC, Wei TY, Chiu YYWTM (1987) Hydrometallurgy 19:209
12. Raju T, Kulangiappar K, Kulandianthan MA, Shankar GK, Muthukumaran A (2005) Electrochim Acta 51:356
13. Chung TD, Park J, Kim J, Lim H, Choi M-J, Kim JR, Chang S, Kim H (2001) Anal Chem 73:3975
14. Kang SK, Chung TD, Kim H (2000) Electrochim Acta 45:2939
15. Shinohara T, Higuchi H, Senba Y, Ohto K, Yoshizuka K, Inoue K (2001) Anal Sci 17:889
16. McMahon G, O’Malley S, Nolan K, Diamond D (2003) ARCHIVOC VII:23
17. Shimojo K, Goto M (2005) Sep Purif Technol 44:175
18. Vataj R, Louati A, Jeunesse C, Matt D (2000) Electrochem Commun 2:769
19. Vataj R, Ridaoui H, Louti A, Gabelica V, Steyer S, Matt D (2002) J Electroanal Chem 519:123
20. Stankovic V, Lassine O, Zonnevijlle F, Comninellis C (submitted) Sep Purif Technol
21. de Groot MT, Koper MTM (2004) J Electroanal Chem 562:81
22. Taguchi S, Feliu JM (2007) Electrochim Acta 52:6023
23. Rondianini S, Vertova A (2004) Electrochim Acta 49:4035
24. Reymond F, Fermin D, Lee HJ, Girault H (2000) Electrochim Acta 45:2647