Pulse Polarographic Studies of the Beryllium – Calcone Complex

by Witold Ciesielski, Sławomira Skrzypek and Michał Kasprzak

Department of Instrumental Analysis, University of Łódź, W. Lindleya 3, 90-131 Łódź, Poland

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Azo-dye, calcone (3-hydroxy-4-[(2-hydroxy-1-naphtyl)-azo]-1-naphthalene sulphonic acid, monosodium salt) and its beryllium complex were studied by differential pulse polarography. It was found, that calcone (calc.) formed an additional cathodic peak in the presence of beryllium ions in ammonium buffer. The peak of the complex was shifted about -200 mV to potentials more negative, than the peak of the free dye. The complex formed was stable and the corresponding complex peak remained constant for an hour. The dependences of peak current on pH and calcone concentration were studied. pH 9.5 was chosen as the most favourable and it was stated that 10-fold excess of dye in relation to beryllium concentration was sufficient to complex all beryllium ions. A possibility of differential pulse polarographic determination of beryllium in the concentration range from $4 \times 10^{-7} \text{ mol l}^{-1}$ to $1.2 \times 10^{-5} \text{ mol l}^{-1}$ was found and the results were processed statistically. The influence of calcium and magnesium, in the presence of EDTA as a masking agent, on peak current of the complex was studied. DC polarographic studies of the complex limiting current in function of mercury column height, and electrocapillary curves of calcone and its beryllium complex were carried out.
od 4 \cdot 10^{-7} \text{ mol l}^{-1} do 1.2 \cdot 10^{-5} \text{ mol l}^{-1} uzyskane wyniki opracowano statystycznie.

Zbadano wpływ wapnia i magnezu w środowisku EDTA jako czynnika maskującego na pik prądu redukcji kompleksu. Z zależności natężenia prądu redukcji kompleksu od poprawionej wysokości słupa rtęci i na podstawie badań odpowiednich krzywych elektrokapilarnych określono charakter prądu redukcji kompleksu.

Azo dyes are widely used in polarographic analysis of metals. Many of them form polarographically active complexes with metals of which direct determination in an aqueous solution is difficult by polarographic or voltammetric method. Beryllium [1] is an representative of these kind of metals.

O-hydroxy-o'-carboxy-azo dyes like Mordant red 60, Mordant red 74 complex beryllium [2] and form electrochemically active complexes. Thorin [3], Beryllon III [4], have been applied in the voltammetric determination of beryllium.

Calcone [5] was used in indirect polarographic procedure which has been developed for measuring micromolar concentrations of magnesium (2 \cdot 10^{-7} \text{ mol l}^{-1}). Calcone is also known as metallochromic indicator in complexometric titration of calcium and magnesium [6,7]. In spite of these applications there is no many information about calcone in chemical literature.

The present paper deals with differential pulse polarographic studies of calcone, its beryllium-complex (log $K_{\text{Be-calc.}} = 12$) [8] and a possibility of using calcone in indirect pulse-polarographic determination of beryllium.

**EXPERIMENTAL**

**Apparatus**

Polarographic measurements were carried out in a three electrode system: a dropping mercury drop electrode as the cathode, a platinum electrode as the anode and a saturated calomel electrode as the reference electrode. Mercury drops at the dropping mercury capillary were dislodged by a magnetic hammer after a required drop time (1 s). A modular microcomputer-controlled universal electrochemical meter (EMU-meter), (Institute of Physical and Theoretical Chemistry, Technical University of Wroclaw, Poland), was employed. The cyclic voltammetry was investigated with the type PA4 polarographic analyzer connected to a hanging mercury drop electrode (HMDE) (Laboratorni Pristroje, Czechoslovakia).

The following equipment was also used: automatic pippets, a pH-meter, type N-517 (Mera-Elwro, Poland), electronic scales, type MC 1 (Sartorius, Germany).

**Reagents**

Standard beryllium solution: 0.1771 g of beryllium sulphate tetrahydrate (Merck, Suprapure®) was dissolved in water with 1 ml of sulfuric acid (96%, Merck, Suprapure®), and the solution was diluted to 100 ml. This $1 \times 10^{-2} \text{ mol l}^{-1}$ stock solution was further diluted as required.

Magnesium solution: 0.2032 g magnesium chloride heksahydrate (analytical grade, POCh, Poland) was dissolved in water and the solution was diluted to 0.1 l. This stock solution was further diluted as required.

Calcium solution: 0.2364 g calcium nitrate tetrahydrate (Merck, Suprapure®) was dissolved in water with 0.1 ml nitric acid (65%, Merck, Suprapure®) and the solution was diluted to 0.1 l. This stock solution was further diluted as required.
Standard copper (II) solution: 0.2497 g of copper (II) sulphate pentahydrate (analytical grade, Riedel-De Haën, Seche-Hannover) was dissolved in water with 0.1 ml sulfuric acid (96%, Merck, Suprapure®) and the solution was further diluted to receive 1 x 10^{-4} mol l^{-1} solution.

Calconce was purchased from Aldrich Chemical Company. It was purified according to paper [6]. Stock calconce solution was prepared by dissolving weighed portions (0.2 g) in water in 250 ml volumetric flasks. Exact titre was determined by copper (II) spectrophotometric titration [6] at 535 nm. This stock solution was further diluted to concentration (1 x 10^{-3} mol l^{-1}). The solution was stable for two weeks.

Ammonium buffers, \(c (\text{NH}_3\cdot\text{HCl} + \text{NH}_3\cdot\text{H}_2\text{O}) = 1 \text{ mol l}^{-1}\) were prepared by addition of hydrochloric acid to ammonia. Ammonia and hydrochloric acid (analytical grade, POCh, Poland) were purified by microdiffusion.

Acetate buffers, \(c (\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH}) = 1 \text{ mol l}^{-1}\), were prepared by addition of sodium hydroxide to acetic acid. Sodium hydroxide and acetic acid (POCh, Poland) were of analytical grade too.

Ethylenediaminetetraacetic acid disodium salt (EDTA), 2.5 x 10^{-2} mol l^{-1} solution: 2.3265 g of EDTA was dissolved in water and the solution was diluted to 250 ml.

Doubly distilled water from glass was used in all experiments. All solutions were stored in polyethylene bottles (HDPE or LDPE, Nalgene, USA) and contact between the solutions and glass vessels was avoided as much as possible.

**Procedure**

Transfer 5 ml EDTA solution, 2.5 ml ammonium buffer, calconce solution, beryllium solution into 25 ml quartz standard flask and dilute to the mark with water. Pour a part of the solution into a quartz polarographic cell and purge with argon for 15 min. Record a polarogram starting the potential scan at 0 V in half an hour since the beryllium has been added.

**RESULTS AND DISCUSSION**

**Preliminary experiments**

The preliminary experiments involved recording of calconce and calconce-beryllium DP polarograms in ammonium buffers (pH 7.9–10.2) and acetate buffers (pH 4.5–5.5). It was found that calconce was reduced at HMDE yielding a polarographic peak. Peak potential was linearly dependent on pH and could be represented by the equation: \(E_p(\text{mV}) = -63 \text{ pH} + 35\). In the presence of beryllium ions in ammonium buffer the peak of the free dye decreased and a new peak appeared at a more negative potential (Figure 1). pH influence on peak potential of the complex gives the following relationship: \(E_p(\text{mV}) = -46 \text{ pH} - 354\). No additional peak was observed in acetate buffer.

It was found that the influence of pH on peak current was negligible and therefore pH 9.5 was adopted in further measurements.

Also the proper dye concentration is important. The dependence of reduction current of the complex on concentration of calconce being in excess was examined too. It was found that dye concentration equal to 8 x 10^{-5} mol l^{-1} is high enough to complex beryllium at concentration 8 x 10^{-6} mol l^{-1} (Fig. 2). In further experiments, 10-fold excess of ligand was used.

The time of the formation of the complexes in alkaline medium was estimated to be 30 min.
Figure 1. DP polarograms of calcone (a) and calcone-beryllium complex (b) in ammonium buffer pH 9.5; $c_B = 0.1$ mol l$^{-1}$; a) $c(\text{calc.}) = 6 \times 10^{-5}$ mol l$^{-1}$, b) $c(\text{calc.}) = c(\text{Be}) = 6 \times 10^{-5}$ mol l$^{-1}$

Figure 2. Relationship between complex (Be-calc.) peak current and calcone concentration in ammonium buffer pH 9.5, $c(\text{Be}) = 8 \times 10^{-6}$ mol l$^{-1}$, $c_B = 0.1$ mol l$^{-1}$.

**Character of the beryllium-calcone complex reduction current**

The character of reduction current of Be-calc. complex was investigated by measuring variation of limiting current ($i_\text{l}$) in a function of $h$, corrected height of the mercury column in DC polarography [9]. The equation $i_\text{l} = k \cdot h^p$ [10] and its logarithmic form $\ln i_\text{l} = k' + p \ln h$ is known as a criterion of the character of reduction current. In this case, $p$, the line slope, was calculated using the least squares method and equals $0.74 \pm 0.03$. These findings indicate the mixed, adsorptive-diffusional character of the reduction current of the complex.

**Electrocapillary curves**

As it was stated above, the character of the reduction current is mixed, adsorptive-diffusional. On the other hand calcone as a macromolecule easily adsorbs on the mercury electrodes [5]. This phenomenon is essential enough because it can consid-
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erably influence the character of the process proceeding at the working electrode.

The obtained electrocapillary curves (Fig. 3) confirm adsorption of calcone (curves C, D). The beryllium-calcone complex causes lowering of the surface tension in the same way (curve E). Comparing curves A and B, and curves C and E in Figure 3 it was noticed that the adsorption depends mainly on the ligand in the complex and that beryllium affects the adsorption a little only.

Figure 3b shows the electrocapillary maximum shifted to negative potentials. The conspicuous increase in drop time marked at \( E < -0.7 \) V is connected with the process of electroreduction of calcone in the beryllium complex. The complex peak occurs in this potential region. A similar phenomenon was noticed for magnesium calcone complex [5].

**Figure 3.** Electrocapillary curves: A - 0.1 mol l\(^{-1}\) ammonium buffer + 0.01 mol l\(^{-1}\) EDTA; B - A + 1x10\(^{-5}\) mol l\(^{-1}\) Be; C - A + 5x10\(^{-5}\) mol l\(^{-1}\) calc.; D - A + 1x10\(^{-4}\) mol l\(^{-1}\) calc.; E - A + 5x10\(^{-5}\) mol l\(^{-1}\) calc. + 1x10\(^{-5}\) mol l\(^{-1}\) Be

**Relationship between complex peak current and beryllium concentration**

A linear relationship between peak current of the complex and beryllium concentration in the range from 4x10\(^{-7}\) to 1.2x10\(^{-5}\) mol l\(^{-1}\) was found. The samples were prepared in volumetric flasks (25 ml) containing EDTA as a masking agent, \( c(EDTA) = 0.01 \text{ mol l}^{-1}\), ammonium buffer pH 9.5, \( c(NH_3\cdotHCl+NH_3\cdotH_2O) = 0.1 \text{ mol l}^{-1}\), calcone \( c(\text{calc.}) = 1\times10^{-4} \text{ mol l}^{-1}\), and beryllium ions. The components were added in the mentioned order. After stirring the samples were transfered to polarographic cells. Oxygen was removed by passing argon for 15 min. The solutions contained no other depolarizers. DP polarographic curves were recorded from -0.6 V to about -1 V vs. SCE in half an hour time, after beryllium was added. The results were processed statistically and it was found that the relative standard deviation was \( s_r \leq 10.6\% \).

**Effect of calcium and magnesium on the beryllium-calcon complex**

Due to the fact that calcone is adopted as metallochormic indicator for the titration of calcium, at higher pH range [6], log \( K_{Ca\text{-calc.}} = 5.58 \) [7], and magnesium, a log \( K_{Mg\text{-calc.}} = 7.64 \) [7], the effect of calcium and magnesium on the peak beryllium-
calcone complex was studied. EDTA as an masking agent was added. The effect of EDTA concentration ($2 \times 10^{-4} - 1 \times 10^{-2}$ mol $\text{l}^{-1}$) on peak height was examined earlier. It was stated, that $1 \times 10^{-3}$ mol $\text{l}^{-1}$ EDTA decreased the blank sample [$c(\text{calc.}) = 1 \times 10^{-4}$ mol $\text{l}^{-1}$] and did not affect the height of the Be-calc. peak. EDTA at concentration of $1 \times 10^{-2}$ mol $\text{l}^{-1}$ decreases the height of the complex peak slightly but doesn’t influence the linearity of the relationship between peak height and beryllium concentration.

The influence of calcium and magnesium was studied with $4 \times 10^{-6}$ mol $\text{l}^{-1}$ beryllium and $1 \times 10^{-2}$ mol $\text{l}^{-1}$ EDTA, and $1 \times 10^{-5}$ mol $\text{l}^{-1}$ beryllium and $1 \times 10^{-2}$ mol $\text{l}^{-1}$ EDTA in the samples. The obtained DP polarograms showed that even a 100 – fold excess of calcium (or magnesium) does not impede the polarographic determination of beryllium.

Conclusions

The observed new peak of Be-calc. complex and the obtained results of DPP and DCP studies show a possibility of using this complex for beryllium determination by adsorptive stripping voltammetry (AdSV).

The influence of others ions on peak current of the complex was limited to magnesium and calcium only, as calcone is an metallochromic indicator in complexometric titration of these ions. Calcone is not a selective reagent, so a possibility of complexing other ions should be taken into account during determination of beryllium in natural samples.

REFERENCES

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