Diethyldithiocarbamates in extraction stripping polarography

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Cadmium determination by stripping polarography has been studied in a benzene—methanol medium of 1 : 1 volume ratio, after Cd^{2+} extraction in the form of diethyldithiocarbamate (the double preconcentration method). Maximum current, corresponding to stripping peak I_p, is proportional to the concentration. The method provides accurate results with a 3—9 % relative standard deviation for $c(Cd^{2+}) = 1 \times 10^{-6}$—$1 \times 10^{-8}$ mol dm^{-3}. Through the analysis of a model mixture of Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+} it was proved that complete separation and separate Cu determination were possible and it was found that electrochemical properties of complexes were of decisive importance in polarographic stripping analysis.

Изучено определение кадмия методом полярографии с накоплением в среде бензол—метанол (соотношение объемов 1 : 1) после экстракции Cd^{2+} в виде диэтилдитиокарбамината (метод двойного концентрирования). Плотность тока пика I_p, принадлежащего анодному окислению, пропорциональна концентрации. Метод дает правильные результаты, коэффициент вариации 3—9 % для $c(Cd^{2+}) = 1 \cdot 10^{-6}$—$1 \cdot 10^{-8}$ моль дм$^{-3}$. Анализом модельной смеси Cu^{2+}, Pb^{2+}, Cd^{2+} и Zn^{2+} проверена возможность полного разделения и отдельного определения Cu и подтверждено, что для полярографии с накоплением являются решающими электрохимические свойства комплексов.

Analyzing complicated complex systems and determining trace quantities of species require the employment of novel effective physicochemical separation and detection methods. Very promising seems to be their combination in the form of hybrid techniques [1]. Using a convenient separation method, a markedly increased selectivity, often with the preconcentration of the to-be-determined component can be achieved.

The employment of extraction in electrochemical stripping analysis is usually associated with reextraction into aqueous phase or involves mineralization of the organic phase. Not many are the data on direct determination in a nonaqueous phase. Some details on determining Au, Sb, Bi, and Sn, after extraction, in the form

of ion associates have been published [2—6]. The use of stable chelates has been limited by the reduction potential range. According to [7], difficulties connected with this may be overcome by influencing the stability constant or by ligand exchange [8] or, possibly, by the exchange of the metal to be determined [7, 9] in the extracted complex. These papers reported separation of Ag, Pb, Cd, and Zn dithizonates. It is also known that 8-hydroxyquinoline has been employed to determine copper [10] when, at the same time, the separation of its complex [11], as well as that of copper(II) diethyldithiocarbamate [12], has been described by the above technique.

The present paper studies a possible application of sodium diethyldithiocarbamate (cupral, $(Et_2dtc)Na \cdot 3H_2O$) — a widely used chelate-forming extraction agent — in the stripping polarography of Cu, Pb, Cd, and Zn. Because of the simplicity of the stripping process the determination conditions have been studied in more detail for $Cd(Et_2dtc)_2$ the electrochemical analysis of which is significant also in view of the difficulty of the determination by absorption spectral methods.

Experimental

$Cd(Et_2dtc)_2$, prepared by precipitating $CdCl_2$ aqueous solution ($c = 1 \times 10^{-2}$ mol dm^{-3}) by an equivalent quantity of cupral, was recrystallized from benzene. Its purity was proved by elemental analysis.

All the remaining chemicals and solvents were anal. grade commercially obtained materials (Lachema, Brno).

Aqueous solutions were prepared in redistilled water, Cd^{2+}, Pb^{2+}, and Zn^{2+} having been extracted from aqueous solutions of the respective nitrates or from an ammonium citrate buffer solution (pH = 5.5), and Cu^{2+} from an HCl solution ($c = 0.1$ mol dm^{-3}). Extraction procedure: 5 cm^3 of cupral aqueous solution ($c = 5 \times 10^{-4}$ mol dm^{-3}) and 15 cm^3 of benzene were added in a 100 cm^3 separating funnel to 50 cm^3 of the to-be-determined ion aqueous solution (for metal concentration under 1×10^{-7} mol dm^{-3} the added amount of cupral was 10 times less). After 3 min the mixture was being hand-agitated for 2 min. After phase separation, the 12.5 cm^3 benzene layer was transferred with a pipette into an electrolytic cell and the same volume of methanol was added.

Ionic strength I of all the solutions was adjusted to 0.1 mol dm^{-3} with sodium perchlorate (dehydrated $NaClO_4$ was used for nonaqueous media).

Measurements were made with a polarograph, Type OH-102 (Radelkis, Budapest). The electrolytic cell of cylindrical shape was one from the set of the Rotating Disc Electrodes (Laboratorní přístroje, Prague). A hanging mercury-drop electrode (HMDE) of the Kemula E-69 b type (Radiometer, Copenhagen), of mercury mass-specified radius $r = 0.373$ mm, and partly also a mercury-film electrode (MFE) on a rotating platinum contact, prepared directly during Cd complex electrolysis at − 1.4 V by the mercury deposition from the $Hg(NO_3)_2$ solution ($c = 5 \times 10^{-5}$ mol dm^{-3}) [13] were used as indicating electrodes. A constant scan rate of 0.1 V s^{-1} was maintained throughout the operation. The reference

electrode consisted of a calomel electrode in an aqueous LiCl solution ($c = 4$ mol dm^{-3}) with a salt bridge filled with an $NaClO_4$ solution ($c = 0.1$ mol dm^{-3}) in a 1:1 benzene—methanol mixture for nonaqueous media or with an aqueous $NaClO_4$ solution ($c = 0.1$ mol dm^{-3}) for aqueous media. It had a potential of $+0.025$ V *vs.* SCE. The auxiliary electrode was a large-surface platinum electrode. The stirrer was made up of a teflone cylinder with a spirally cut surface.

Inert gas employed was argon which in nonaqueous media was saturated with the vapours of the solvent. Electrolytic process: Electrolysis took place at a potential of -1.4 V 20 s after mixing had started. Then mixing was stopped and after 30 s an anodic stripping polarogram was recorded.

Results and discussion

$Cd(Et_2dtc)_2$ *Electrolysis*

A $Cd(Et_2dtc)_2$ solution ($c = 1 \times 10^{-6}$ mol dm^{-3}) was investigated. Stripping Cd peak recorded both at an HMDE and at an MFE was sufficiently sharp and corresponded to the potential $E_p = -0.30$ V (Fig. 1).

The graph of maximum current I_p dependence on the electrolytic preconcentration potential in the range of -0.9 to -1.4 V was of wave form reaching a limit value at -1.3 V. The wave is characterized by the values $E_{1/2} = -0.97$ V, $(\alpha z_a) = 0.5$. The latter value proves that the redox process is irreversible. Anodic Cd peak current grew linearly with accumulation time (from 2 to 8 min).

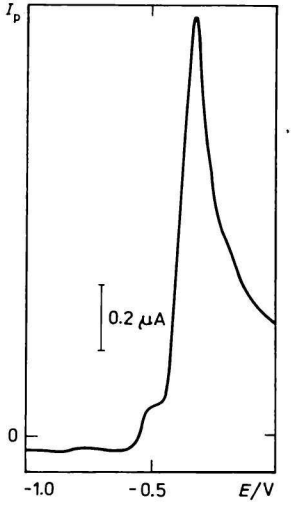

Fig. 1. Stripping Cd voltammogram recorded at an HMDE, $Cd(Et_2dtc)_2$ solution ($c = 1.66 \times 10^{-6}$ mol dm^{-3}); benzene—methanol in volume ratio of 1:1, $c(NaClO_4) = 0.1$ mol dm^{-3}; $E_{el} = -1.2$ V *vs.* 4 M-CE; electrolytic accumulation time: 2 min.

The size of the mercury drop was controlled by means of a graduated scale, marked on the piston of mercury bin of the commercially obtained electrode used. Given that scale divisions and the volume of the ejected drop are directly proportional, its radius increases nonlinearly on condition that it is spherical in shape ($r = (0.75 \cdot V/\pi)^{1/3}$), and it was found that maximum current I_p was proportional to this radius (correlation coefficient $r = 0.960$).

Maximum current I_p dependence on $Cd(Et_2dtc)_2$ concentration ($c = 4 \times 10^{-8}$ to 9×10^{-7} mol dm^{-3}) was linear (correlation coefficient $r = 0.994$, sensitivity being 0.75 A dm^3 mol^{-1}). Accumulation time used at a -1.4 V potential was 2 min and at concentrations under 1×10^{-7} mol dm^{-3} blank experiment current values were read off. In a similar Cd^{2+} determination in an aqueous medium of concentration range between 1×10^{-8} and 1×10^{-6} mol dm^{-3}, after electrolysis at a -0.9 V potential, *i.e.* 0.3 V higher than $E_{1/2}$, the sensitivity was found to be 0.80 A dm^3 mol^{-1} (correlation coefficient $r = 0.995$). Peak current signal, therefore, measured in a nonaqueous medium, is analytically utilizable and, at the same time, represents a certain decrease in sensitivity compared with that in an aqueous solution (by 6 % on the values given above).

Extraction and Cd^{2+} determination

A relatively high formation rate of dithiocarbamate metal complexes under study, as well as the effect of the solution pH value on their formation and extraction, has been reported in [14, 15].

Employing stripping polarography in phase analysis after agitating 25 cm^3 of benzene $Cd(Et_2dtc)_2$ solution ($c = 1 \times 10^{-5}$ mol dm^{-3}) with 25 cm^3 of water (or possibly citrate buffer solution — pH = 5.5) it was found possible to determine distribution ratio value d (ratio of equilibrium complex concentrations in benzene and aqueous phase, respectively) for $Cd(Et_2dtc)_2$, *viz.* $d = 250 \pm 20$.

The Et_2dtc^- anion itself yields an anodic peak caused by electrode material oxidation in the presence of the complex-forming agent, both in an aqueous and in a nonaqueous solution at -0.5 V [16]. Since, however, an undissociated protonized form of ligand, which at pH > 5 is but in low concentration ($pK_a = 3.4$) [15] has been extracted into benzene, the presence of a free ligand on the stripping polarogram of the extract has been manifested only to a small extent as a prepeak of peak Cd. This was mostly the case of the ligand liberated during the electrolytic decomposition of the complex. In dissolving Cd into a benzene—methanol solution as well as into an aqueous solution, both containing larger addition of cupral, a decrease in maximum current I_p has been recorded as well as a shift of the peak to positive potential values. An opposite shift of E_p should be expected for Cd oxidation in a complex-forming medium; the observed effects may be explained as being due to the blocking of the electrode surface by mercury complexes.

Precision and accuracy in determining Cd by the extraction stripping polarography technique have been verified for the initial $CdCl_2$ solution concentrations ($c = 1 \times 10^{-8}$ — 1×10^{-6} mol dm^{-3}) made in parallel series (m amounts of extracts per n determinations). The precision of the method is given by standard deviations s_n and $s_{m,n}$ [17] as follows: for $CdCl_2$ solution ($c = 1 \times 10^{-6}$ mol dm^{-3}), relative standard deviation $s_{4,3\,rel}$ represents 2.6 %; for $CdCl_2$ solution ($c = 1 \times 10^{-7}$ mol dm^{-3}), $s_{4,4\,rel}$ represents 9.1 % and for $CdCl_2$ solution ($c = 1 \times 10^{-8}$ mol dm^{-3}), $s_{3,3\,rel}$ represents 6.9 %. These values are comparable with the usually obtained precision values in stripping polarography. Variance in the results is not due to the combination of extraction and stripping polarography as evidenced by values s_n being close to the respective $s_{m,n}$ values.

The graph of dependence of maximum current, corresponding to dithiocarbamate extraction stripping peak I_p on the $CdCl_2$ initial concentration ($c = 1 \times 10^{-8}$ — 1×10^{-6} mol dm^{-3}) was linear throughout. Using maximum current dependence on $Cd(Et_2dtc)_2$ concentration, we have attached to each separate value I_p the found quantities of Cd ($m_{Cd,\,found}$) which we compared with the amounts of Cd taken ($m_{Cd,\,taken}$) for analysis (in aqueous solution). They are linearly dependent (correlation coefficient $r = 0.9996$) and the coefficients of the equation

$$m_{Cd,\,found} = a + b \cdot m_{Cd,\,taken}$$

calculated by regression analysis are: $a = (-3.14 \pm 13.56) \times 10^{-8}$ g, $b = 0.999 \pm 0.023$. The accuracy of the method has been confirmed by the a and b values and by their confidence intervals.

The feasibility of raising the overall sensitivity of the method by preconcentrating Cd^{2+} from a sample of a larger volume has also been tested. In a 500 cm^3 separating funnel, Cd^{2+} ($c = 1 \times 10^{-8}$ or 1×10^{-7} mol dm^{-3}) has been extracted from a 450 cm^3 aqueous solution, keeping to the procedure described in Experimental. Cd losses, after its value has been determined by the stripping polarography process, amounted to 4—10 % of the quantity taken, which is comparable with those sustained in some of the above-described experiments. Cd extraction stripping polarography thus represents a method of double preconcentration.

Ion mixture analysis

To investigate further possible utilization of dithiocarbamates we have chosen a model mixture containing Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+} ions, as such a system is often being analyzed in practice by the stripping voltammetry technique and the diethyldithiocarbamate complexes of these ions represent a selection of chelates of varied stability and electrochemical properties.

The mixture was divided as described in Ref. [14] on the basis of complex formation dependence on pH. Cu^{2+} was extracted in complex form from the HCl

($c = 0.1$ mol dm^{-3}) solution. No copper content was detected in the aqueous phase after extraction. In the nonaqueous medium the Cu peak was observed to have been shifted towards positive potential values just as was the case with Cd (Table 1), its position, as in the determination in the aqueous solution, having been affected by Hg oxidation. Better resolution may be obtained by adding distilled pyridine, after which the Cu peak gets well separated from Hg oxidation at the 0.0 V potential. Pb^{2+}, Cd^{2+}, and Zn^{2+} were determined after aqueous phase pH had been adjusted with NH_3 and ammonium citrate to pH 9.

Table 1

Electrochemical characteristics and stability constants of investigated species (HMDE; potential (V) *vs.* 4 M-CE; $NaClO_4$ aqueous solution ($c = 0.1$ mol dm^{-3}) was used for aquo-ions and $NaClO_4$ solution ($c = 0.1$ mol dm^{-3}) in 1:1 benzene—methanol mixture for complexes; $\log \beta_2$ values determined potentiometrically in $NaClO_4$ solution ($c = 0.1$ mol dm^{-3}) in methanol)

Central ion	Aquo-ion		Complex		
	$E_{1/2,\,red}$/V	$E_{p,\,an}$/V	$E_{1/2,\,red}$/V	$E_{p,\,an}$/V	$\log \beta_2$
Cu(II)	−0.03	−0.02	−0.58	+0.33	23.9
	−0.22		−0.80		
Pb(II)	−0.43	−0.42	−0.81	−0.18	15.5
Cd(II)	−0.63	−0.53	−0.96	−0.29	17.1
Zn(II)	−1.02	−0.97	−1.56	−0.70	15.1

Electroanalytical characteristics of aquo-ions and complexes of Pb, Cd, and Zn (Table 1) were derived from the study of their mixture in aqueous solution (each aquo-ion was of a 1×10^{-6} mol dm^{-3} concentration) or possibly in benzene—methanol after extraction. In a nonaqueous medium stripping curves lie at more positive potentials but their mutual separation has not changed. Table 1 also shows stability constant values of respective complexes obtained by potentiometric titration using a silver indicating electrode in methanolic medium. All these facts lead to the conclusion that the use of diethyldithiocarbamate complexes in stripping polarography is mainly conditioned by their electrochemical properties and is less dependent on their stability constants.

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