DISTURBANCE OF A FILM OF TRITON X-100 ON THE HANGING MERCURY DROP ELECTRODE DURING THE DETERMINATION OF METAL IONS BY ANODIC STRIPPING VOLTAMMETRY

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The effect of electroreduction of Zn(II), Cd(II), Pb(II) and Cu(II) ions on the stability of a film of the surfactant Triton X-100 on the surface of a hanging mercury drop electrode was investigated. A procedure is suggested to disturb the film in order to facilitate the determination of the above metal ions by anodic stripping voltammetry with accumulation.

Triton X-100, a typical polyoxyethylenealkylphenolmonoether, is a widely used surfactant which can be present in surface waters due to its incomplete biodegradation. This surfactant forms a stable film on the surface of a hanging mercury drop electrode[1-4] (HMDE). Such stable films are formed in the case of irreversible adsorption[2,3]. Generally, interfering effects during stripping can be minimized by using the method of replacement of the medium. The stable film of Triton X-100, however, is a source of error in trace element analysis by anodic stripping voltammetry even if this method is applied[4]. The results of ref.[4] provide no information as to whether the stripping process is affected by a carry-over film or not.

The film of Triton X-100 can be disturbed[1] by vigorous stirring of the solution applying an electrode potential which lies above the adsorption region of the surfactant. The present paper examines the possibility of using that approach to disturb the surfactant film during the determination of Zn(II), Cd(II), Pb(II) and Cu(II) by anodic stripping voltammetry.

EXPERIMENTAL

Apparatus

A Radelkis OH-105 polarograph was used. The voltage scan rate was 400 mV min^{-1}, the alternating voltage amplitude was −2 mV. The instrument was augmented with a controlled HMDE equipment (Radelkis) fitted with an additional auxiliary molybdenum electrode. A saturated calomel electrode served as the reference electrode. The glass cell accommodated a small Teflon beaker so that the solution came in contact with Teflon only. The potential was measured with an N-517 digital voltmeter (Mera–Tronic, Poland).

Reagents

Triton X-100 was a commercial chemical (Merck). Sodium sulfate and potassium chloride to be used for the preparation of the base electrolytes were purified by double recrystallization and heating at 600 °C. Aqueous 0.5 M Na_2SO_4 and 0.15 M KCl + 0.05 M CH_3COONa (adjusted to pH 4.7 with CH_3COOH) served as the supporting electrolytes.

Standard solutions of Zn(II), Cd(II), Pb(II) and Cu(II) were prepared conventionally. Working solutions were prepared immediately before measurement.

All solutions were prepared in water which had been triply distilled from quartz. Freshly distilled water was invariably used. All vessels were glass or quartz.

The solutions were thermostatted at 25 °C in the measuring flasks and then placed in the thermostatted (25 °C) measuring cell, where they were deaerated by nitrogen purging.

Procedure

The film of Triton X-100 was obtained by the tensammetric technique with accumulation[1]; the adsorption was conducted from a vigorously stirred solution at −1.4 V for 5 min. The concentration of Triton in the supporting electrolyte used was 1 mg l^{-1}. Desorption of Triton was conducted for 3 min at a potential of −1.75 V after transferring the electrode into a vigorously stirred solution of the pure supporting electrolyte. The tensammetric curve was subsequently recorded in the nonstirred solution in the direction of negative potentials. Alternatively, the electrode was transferred into a corresponding electrolyte solution containing ions of Zn(II) and Cd(II) or Pb(II) and Cu(II). D.C. anodic stripping voltammetry with accumulation was applied; the concentration of each metal was $5 . 10^{-7}$ mol l^{-1}, preconcentration time 5 min, preconcentration potential −1.4 V. The metal ions were determined both at a fresh mercury drop and at a mercury drop coated with a Triton X-100 film as described above.

RESULTS AND DISCUSSION

The effect of electroreduction of Zn(II), Cd(II), Pb(II) and Cu(II) ions on the stability of a film of Triton X-100 on the HMDE surface was investigated in both kinds of supporting electrolyte. The preconcentration electrolysis from the supporting electrolyte containing one of the metal ions was performed using the HMDE coated by a Triton film. Thereafter the electrolyte was replaced with the pure supporting electrolyte and the tensammetric peaks of the surfactant were recorded. The measurements revealed that the reduction of any of the metal ions had no effect upon the shape or height of the tensammetric peak of Triton, hence, that the film remained intact.

The method of disturbing the film on the electrode surface, worked out[1] for 0.5 M Na_2SO_4, was also found effective in the solution of 0.15 M KCl + 0.005 M CH_3COONa. After a 3-min vigorous stirring of the solution at −1.75 V, i.e. beyond the region of Triton X-100 adsorption, no tensammetric peak of the surfactant was observed, giving evidence that the film was completely desorbed from the electrode surface.

Further work was aimed at making use of the above method for removing the film from the electrode surface so that its effect on the determination of the metal ions by voltammetry with accumulation be eliminated. Ions of each of the metals: Zn(II), Cd(II), Pb(II) and Cu(II) were determined in triplicate in the potassium chloride–

sodium acetate supporting electrolyte; Zn(II) and Cu(II) were also determined in the sodium sulfate electrolyte. Examples of the voltammetric peaks measured at a fresh electrode, at the electrode coated with a Triton film, and at the same electrode after disturbing the film are shown in Fig. 1. Invariably, the peaks obtained at the film-coated electrode were significantly lower than at the fresh drop. This is demonstrated in Table I by the i_p'/i_p values, which are ratios of the peak current at the coated electrode (i_p') to the peak current at the fresh electrode in the pure supporting electrolyte (i_p): the ratios are considerably lower than unity. On the other hand, the peaks obtained at the same mercury drop in the pure supporting electrolyte resembled those observed at the

TABLE I
Values of the ratios of the peak current at a film of Triton X-100 i_p' and after destruction of the film i_p'' to the peak current at a fresh mercury drop i_p

Metal ion	Supporting electrolyte (pH)	i_p'/i_p	i_p''/i_p
Zn(II)	0.15 M KCl + 0.05 M CH_3COONa (4.7)	0.76	0.98
Zn(II)	0.5 M Na_2SO_4	0.38	0.99
Cd(II)	0.15 M KCl + 0.05 M CH_3COONa (4.7)	0.62	0.99
Cd(II)	0.5 M Na_2SO_4	0.54	0.98
Pb(II)	0.15 M KCl + 0.05 M CH_3COONa (4.7)	0.67	1.06
Cu(II)	0.15 M KCl + 0.05 M CH_3COONa	0.74	1.00

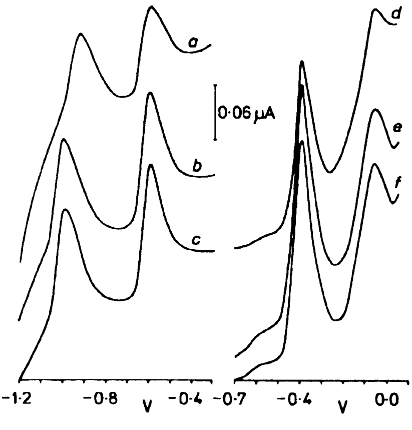

FIG. 1
Peaks of Zn(II) and Cd(II) (*a*, *b*, *c*), Pb(II) and Cu(II) (*d*, *e*, *f*): at a film of Triton X-100 (*a*, *d*); after destruction of the film (*b*, *e*) and at a fresh mercury drop (*c*, *f*). Supporting electrolyte: 0.15 M KCl + 0.05 M CH_3COONa (pH 4.7)

fresh, uncoated electrode; the ratios of the peak current after disturbing the film (i_p'') to the peak current at a fresh mercury drop (i_p) oscillate about unity (Table I). This permits us to claim that the developed method of disturbing the Triton film on the electrode surface, consisting in its desorption at a suitable potential lying beyond the adsorption region combined with a vigorous stirring of the replaced electrolyte, can be used to facilitate the determination of Zn(II), Cd(II), Pb(II) and Cu(II) by anodic stripping voltammetry with accumulation.

REFERENCES

1. Pawlak M. K.: Collect. Czech. Chem. Commun. *56*, 78 (1991).
2. Sawamoto H., Tanoue Y.: J. Electroanal. Chem. *181*, 209 (1984).
3. Sawamoto H., Gamoh K.: J. Electroanal. Chem. *283*, 421 (1990).
4. Florence T. M., Mann K. J.: Anal. Chim. Acta *200*, 305 (1987).
5. Lukaszewski Z., Batycka H., Zembrzuski W.: Anal. Chim. Acta *175*, 55 (1985).

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