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Investigations on adsorption potentiometry

Part VI. Derivative adsorption chronopotentiometry of furazolidone

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Abstract

An electroanalytical method for the determination of trace-amounts of furazolidone, based on derivative chronopotentiometry of furazolidone accumulated adsorptively on the surface of a hanging mercury drop electrode, has been developed The dependences of the peak current of reduction of adsorbed furazolidone on the preconcentration time and the preconcentration potential are discussed The electrode reaction was found to be totally irreversible Optimum experimental conditions include $9\,0 \times 10^{-3}$ mol l^{-1} KOH and a preconcentration potential of $-0\,30$ V (vs SCE) Under these conditions, the detection limit and the linear range are $1\,0 \times 10^{-10}$ and $3\,4 \times 10^{-9}$–$1\,4 \times 10^{-6}$ mol l^{-1}, respectively, for an accumulation time of 60 s The method was applied to samples of furazolidone tablets

Keywords Potentiometry, Furazolidone, Stripping analysis

Furazolidone, 3-(5-nitrofurfurylideneamino)-2-oxazolidone, is a synthetic nitrofuran derivative with a nitro group at the 5-position on the furan ring It has been widely used in the treatment of caecal coccidiosis in chickens and necrotic enteritis in swine It is generally added to animal feeds to prevent various poultry and swine diseases In man this drug is therapeutically effectively as an antibacterial and bactericidal agent

Furazolidone has been determined by liquid chromatography [1,2], thin-layer chromatography [3], spectrophotometry [4], colour reactions [5], turbidimetry [6] and polarography [7–10], but little attention has been paid to the polarographic determination of furazolidone Vignoli et al [10] found that the Ilkovic equation was obeyed for 10–40 μg ml^{-1} of furazolidone and the practical limit of determination was 5–10 μg ml^{-1} Morales et al [7] determined furazolidone polarographically in pyridine–formic acid buffer (pH 4 5) containing 0 1 mol l^{-1} tetramethylammonium chloride The calibration graph was rectilinear from $1\,24 \times 10^{-6}$ to $5\,88 \times 10^{-3}$ mol l^{-1} and the detection limit was $1\,24 \times 10^{-6}$ mol l^{-1}

There has been increasing interest in adsorptive accumulation measurements, known as adsorption voltammetry of trace organic and inorganic substances that cannot be accumulated by electrolysis [11,12] More recently, an ultra-trace electroanalytical method for the determination of inorganic ions, e g , iron, bismuth and beryllium, called derivative adsorption chronopotentiometry has been proposed This method is similar to chronopotentiometric stripping analysis, and its theory has been reported [13–16] In this method, instead of electrolytic accumulation, inorganic complexes can be accumulated by adsorption and the derivative of time with respect to potential is

then recorded Up to now, derivative adsorption chronopotentiometric of organic substances has not been reported

In this work, the derivative adsorption chronopotentiometric determination of furazolidone at a hanging mercury drop electrode (HMDE) was developed The method was applied to samples of tablets and urine

EXPERIMENTAL

Apparatus

A Model DPSA-3 stripping analyser (Shandong Seventh Electronic Factory) for derivative adsorption chronopotentiometry or a Model 79-1 voltammetric analyser (Jinan Fourth Radio Factory) for linear or cyclic adsorption voltammetry coupled with a Model LZ_s-200 X–Y recorder (Shanghai Dahua Instrument Factory) was used in connection with a cell, using potentiostatic control of the electrode potential by means of a three-electrode system consisting of a Model SH-84 HMDE (Department of Chemistry, Shandong University) as the working electrode, a platinum plate as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode, connected to the analyte In the preconcentration step, the solution was stirred with a PTFE-coated stirring bar, rotated by a Model 78-1 magnetic stirrer (Nanhui Telecommunication Equipment Factory)

Reagents and solutions

A ca 10^{-2} mol l^{-1} stock standard solution of furazolidone was prepared by dissolving the appropriate amount of furazolidone (> 99%) in N, N-dimethylformamide (DMF) The solution was stored in the dark Working standard solutions were obtained by diluting the stock standard solution with water Other reagents were of analytical-reagent grade and all solutions were prepared with doubly distilled water

Procedure

The supporting electrolyte consisted of 9×10^{-3} mol l^{-1} KOH The solution was deaerated for 10 min with pure nitrogen The measurements were carried out after a preconcentration step in which the solution was usually stirred for 60 s at a preconcentration potential, E_a, of −0 30 V (vs SCE) For derivative adsorption chronopotentiometry, after a rest period of 30 s, the potentiostatic circuitry was disconnected and a constant reducing current, i_0, of 1 μA was passed through the HMDE and the counter electrode The plot of dt/dE vs E was stored in a stripping analyser and subsequently plotted All potentials were measured against the SCE

RESULTS AND DISCUSSION

Adsorptivity and derivative adsorption chronopotentiogram of furazolidone

Figure 1 shows the drop time as a function of potential for solutions with and without furazolidone in 9×10^{-3} mol l^{-1} KOH When DMF is added to the solution, the drop time decreases in the range of −0 05 to −1 2 V, which suggests that the DMF is adsorbed at the mercury elec-

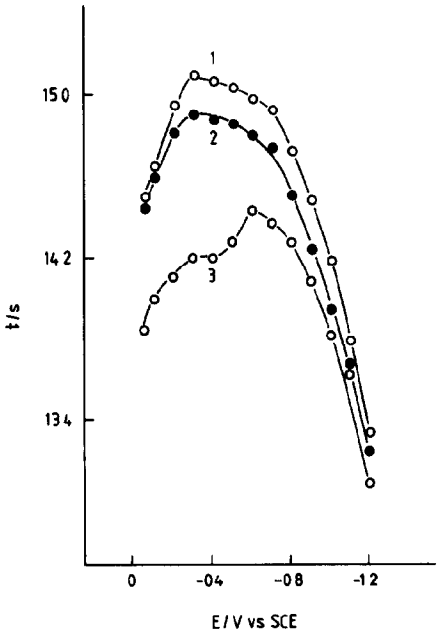

Fig 1 Drop time curves (1) 9×10^{-3} mol l^{-1} KOH, (2) (1) + 2.6×10^{-4} mol l^{-1} DMF, (3) (2) + 3.4×10^{-4} mol l^{-1} furazolidone

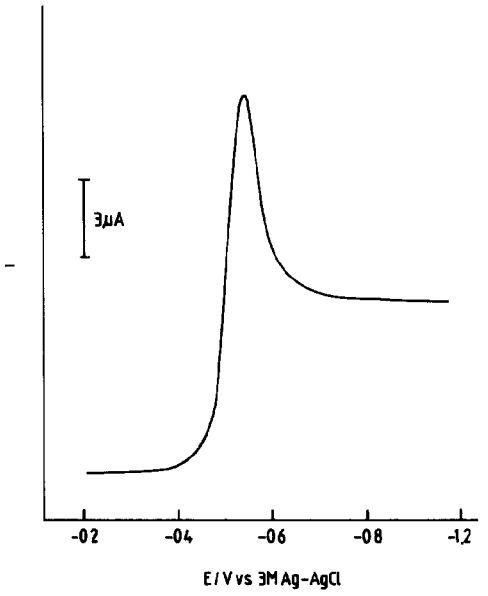

Fig 2 Normal-pulse polarogram for the reduction of furazolidone (9×10^{-3} mol l^{-1} KOH, 1.56×10^{-4} mol l^{-1} furazolidone $t_d = 1$ s, $v = 5$ mV s^{-1}

trode In the presence of furazolidone, the drop time decreases again A peak is observed in the normal-pulse polarogram for the reduction of furazolidone (Fig 2) In 9.0×10^{-3} mol l^{-1} KOH solution, no reduction peak appears on the adsorption voltammogram in the potential range from −0 4 to −1 6 V When 5.2×10^{-5} mol l^{-1} DMF is added to this solution, a peak appears at −1 28 V When a micro-amount of furazolidone is added to a solution containing DMF, a very sensitive peak appears at about −0 60 V (Fig 3) It is obvious that the sensitive peak results from reduction of furazolidone

Typical derivative adsorption chronopotentiograms at different preconcentration times, t_a, are shown in Fig 4 The peak height, $(dt/dE)_p$, increases on extending t_a These features are characteristic of a reaction of adsorbed reactants on the electrode [17–21] The adsorptivity of furazolidone on the surface of the mercury electrode is dependent on the preconcentration potential, E_a The relationship between t_p and E_a is shown in Fig 5 Obviously, the adsorption is strongest at a preconcentration potential of −0 30 V

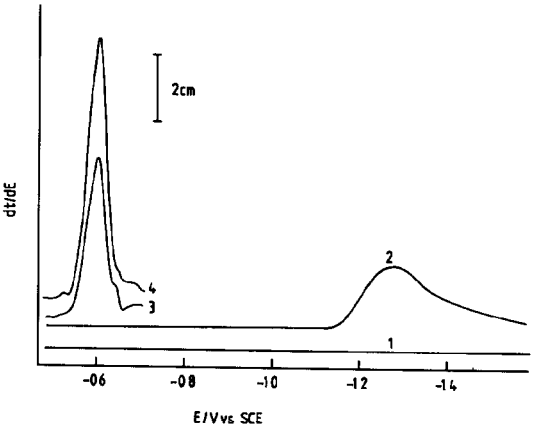

Fig 3 Derivative adsorption chronopotentiograms of furazolidone (1) 9×10^{-3} mol l^{-1} KOH, (2) (1) + 5.2×10^{-5} mol l^{-1} DMF, (3) (1) + 4.8×10^{-8} mol l^{-1} furazolidone, (4) (1) + 7.7×10^{-8} mol l^{-1} furazolidone Sensitivities of the analyser and recorder, 5 and 50 mV cm^{-1}, respectively $E_a = -0.30$ V, $t_a = 60$ s, $i_o = 1.0$ μA

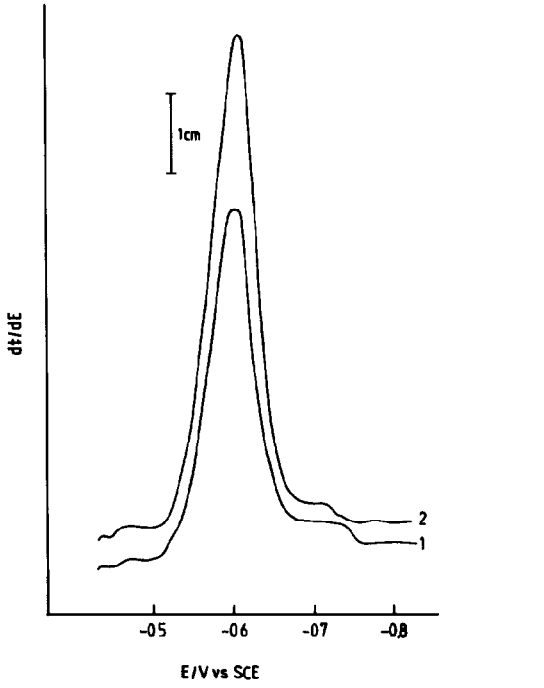

Fig 4 Derivative chronopotentiograms of reduction of furazolidone adsorbed at preconcentration times, t_a, of (1) 30 and (2) 60 s 9×10^{-3} mol l^{-1} KOH, 7.2×10^{-8} mol l^{-1} furazolidone Sensitivities of the analyser and recorder, 10 and 50 mV cm^{-1}, respectively $E_a = -0.30$ V, $i_o = 1$ μA

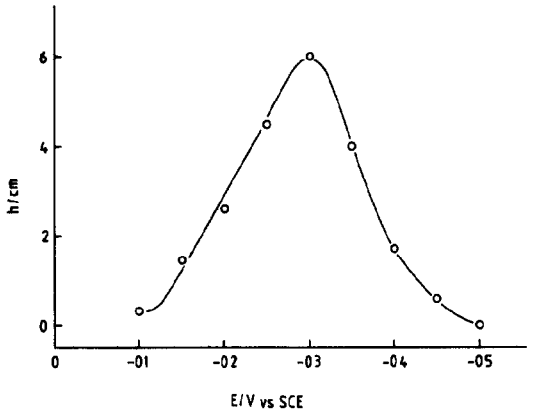

Fig 5 Dependence of the peak current of reduction of adsorbed furazolidone on the preconcentration potential Conditions as in Fig 3

Figure 6 shows the linear sweep cyclic adsorption voltammogram of furazolidone When the potential sweeps negatively from −0 30 to −0 80 V, a reduction peak of furazolidone appears at about −0 55 V When the potential sweeps positively from −0 80 to −0 30 V, no anodic peak

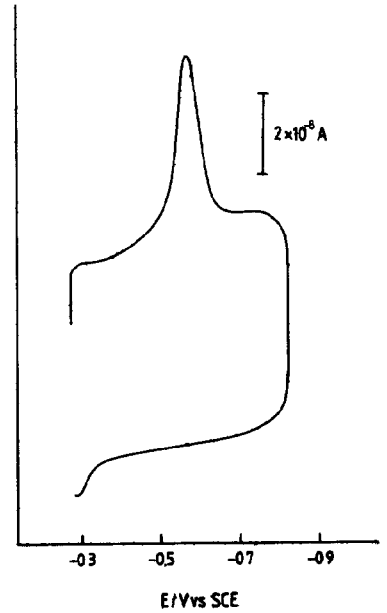

Fig 6 Linear sweep cyclic voltammogram of adsorbed furazolidone 9×10^{-3} mol l^{-1} KOH, 2.8×10^{-7} mol l^{-1} furazolidone $E_a = -0.30$ V, $t_a = 60$ s, $v = 140$ mV s^{-1}

TABLE 1

Results for determination of furazolidone in tablets

Sample	Amount stated (mg)	Amount found (mg)	Recovery (%)
A	100	102	100
B	100	101	92

appears It can be concluded that the interfacial reduction of furazolidone is a totally irreversible process [19]

Analytical application

It was experimentally found that the peak current was dependent on the concentration of the supporting electrolyte, E_a, t_a and the reducing current, i_o, the optimum conditions are 9×10^{-3} mol l^{-1} KOH, $E_a = -0.30$ V and $t_a = 60$ s The smaller is i_o, the larger is the peak height, 1 μA was chosen for subsequent experiments The linear range of derivative adsorption chronopotentiometry of furazolidone is 3.4×10^{-9}–1.4×10^{-7} mol l^{-1} and the limit of detection is 1.0×10^{-10} mol l^{-1}, respectively, for a preconcentration time of 60 s

About 0 04 g of powdered furazolidone tablets was dissolved in DMF, transferred into a 10-ml volumetric flask and diluted to the mark with DMF A 50 μl volume of solution was transferred into a 25-ml volumetric flask, then 50-μl aliquots were taken and added to 25 ml of 9×10^{-3} mol l^{-1} KOH solution and analysed by applying the standard addition method

The results are summarized in Table 1 The recovery of added furazolidone was 92–100%

TABLE 2

Results of determination of furazolidone in urine at different times [a]

Sample A		Sample B	
Time (h)	$(dt/dE)_p$ (cm)	Time (h)	$(dt/dE)_p$ (cm)
0	3 25	0	3 00
24	3 25	24	2 85
48	3 25	48	2 80

[a] 9×10^{-3} mol l^{-1} KOH, 6.2×10^{-8} mol l^{-1} furazolidone, other experimental conditions as in Fig 3

The results for the determination of furazolidone are in agreement with the stated contents It was experimentally found that furazolidone was stable in urine for more than 48 h (see Table 2) It is possible to determine micro-amounts of furazolidone in urine by this method

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