Monatshefte für Chemie 125, 497–507 (1994)

Monatshefte für Chemie
Chemical Monthly

Voltammetric Determination of As(III) in an Aqueous Zwitterionic Complexing Medium

H. A. Azab*, S. A. El-Shatoury, and **N. Abo El-Maali**

Department of Chemistry, Faculty of Science, Assiut University, Assiut, Egypt

Summary. The polarographic behaviour and determination of As(III) in aqueous complexing electrolytes (bicine buffer solutions) of *pH* values varying from 1.13–11.96 have been investigated at 25 °C (direct current and differential pulse polarographic techniques). Using DC polarographic measurements, it was shown that reduction of As(III) takes place along one or three waves depending upon the *pH* value of the solution. Microcoulometric experiments have been performed at the limiting region of the different waves obtained at different *pH* values. Cyclic voltammograms were recorded using a HDME to investigate the nature of reduction. Schemes for the mechanism of reduction occurring at the DME have been deduced. Kinetic parameters and wave characteristics for the reduction of As(III) have been calculated. A method for DPP determination of As(III) in bicine buffer solution of *pH* 1.41 is reported. The detection limit of the method is 6.60×10^{-8} *M* As(III).

Keywords. Voltammetry; Polarography; Coulometry; Arsenic; Bicine.

Voltammetrische Bestimmung von As(III) in einem wäßrigen zwitterionischen komplexierenden Medium

Zusammenfassung. Das polarographische Verhalten und die polarographische Bestimmung von As(III) in wäßrigen komplexierenden Elektrolyten (Bicin-Pufferlösungen) wurde bei *pH*-Werten zwischen 1.13 und 11.96 und 25 °C untersucht (Direktstrom- und Differentialpulstechniken). Mittels DC-Polarographie wurde gezeigt, daß die Reduktion von As(III) je nach dem *pH*-Wert der Lösung in einer oder in drei Wellen erfolgt. In den Grenzbereichen der bei verschiedenen *pH*-Werten erhaltenen unterschiedlichen Wellen wurden microcoulometrische Experimente durchgeführt. Zur Untersuchung des Reduktionsvorgangs wurden cyclische Voltammogramme unter Verwendung einer HDME durchgeführt. Für den Mechanismus der an der Quecksilbertropfelektrode stattfindenden Reduktion wurden Reaktionsgleichungen ermittelt. Kinetische Parameter und Wellencharakteristika für die Reduktion von As(III) wurden berechnet. Eine Methode zur Bestimmung von As(III) mittels differentieller Pulspolarographie in Bicin-Pufferlösung bei *pH* 1.14 wird vorgestellt. Die Erfassungsgrenze der Methode liegt bei 6.60×10^{-8} *M* As(III).

Introduction

The determination of the content of arsenic in biological and industrial specimens has been considered adequate to assess the presence, amount, and behaviour of this element. Numerous titrimetric and polarographic methods have been cited in the literature [1–16]. In most supporting electrolytes studied the reduction of arsenic gives rise to complicated waves unsuitable for analytical work. There are, however, a few media in which well defined polarographic reduction waves are produced. This prompted us to study the polarographic behaviour and determination of arsenite ions in bicine buffer solutions using DC and DPP techniques in continuation of our work on the polarographic reduction and determination of oxygenated anions [17, 18] in aqueous solutions.

Experimental

All chemicals used were of analytical grade (BDH) product.

A stock 0.0145 *M* sodium arsenite solution was prepared by dissolving the required amount of $NaASO_2$ in bidistilled water. The resulting solution was then standardized by the bromate method [19]. Solutions of lower concentrations were then prepared by accurate dilutions. Bicine buffer solutions were prepared as recommended [20].

DC polarographic measurements were carried out with a Tacussel PRG3 apparatus equipped with three Tacussel RMO6 electrodes and a thermostated cell. A saturated calomel electrode served as the reference electrode. The dropping mercury working electrode had the following characteristics: $m = 3.264\,\mathrm{mg\,s^{-1}}$ and $t = 4.455\,\mathrm{s\,drop^{-1}}$. The height of the mercury column was adjusted at a level of 50 cm allowing a proper drop. DPP measurements and cyclic voltammograms were carried out with an EG & G Model 264A polarographic analyzer coupled with a RE0089 x–y recorder. The working electrode was a PAR 303A SMDE (medium size drop) with an area of $0.017\,\mathrm{cm^2}$ equipped with a platinum auxiliary electrode and an Ag/AgCl/saturated KCl reference electrode.

Procedure

An aliquot of 10 ml of the supporting electrolyte (0.01 *M* bicine) was deaereated with purified nitrogen for 12 min. The arsenite ions were then introduced into the cell solution and polarograms or cyclic voltammograms were recorded. The following parameters have been imposed: drop time, 1 s; scan rate, 5 mV/s; pulse amplitude for DPP, 50 mV; a scan rate for CV, 100 mV/s. For all measurements, an equilibrium time of 15 s was applied before recording the polarograms or voltammograms. By use of a calibration curve, the concentration of As in unknown samples could be determined.

Results and Discussion

Current Potential Curves

The DC polarographic behaviour of 0.5 m*M* sodium arsenite in bicine buffer solutions of *pH* varying from 1.13 to 11.96 is represented by the polarograms shown in Fig. 1. The results show that the reduction of arsenite ions occurs along three steps at *pH* values 1.13, 2.03, and 2.52. At *pH* values 1.13 and 2.03, the second and third waves seem to be intermingled waves. At *pH* 1.51 only one reduction wave was observed, while at pH 6.0 the arsenite reduction wave is masked by the hydrogen wave which immediately follows. No reduction waves for As(III) have been obtained in the *pH* range 3.0–6.0. It has been claimed that polarographic reduction of As(III) does not occur in neutral solutions [4], but in the presence of weak acids (acetic, phosphoric) in the supporting electrolyte reduction occurs and a maximum appears on the polarogram. In the *pH* range 7.0–9.51 the three wave pattern is replaced by a single well developed wave shifted to a more negative potential. The disappearance of a maximum in the neutral medium may be attributed to the adsorption of the

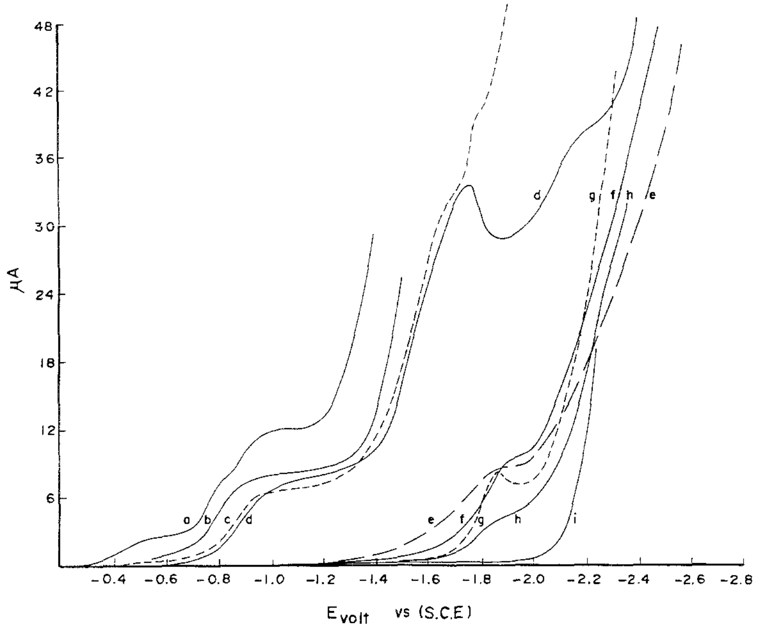

Fig. 1. Polarograms of 5×10^{-4} *M* As(III) in bicine buffer solutions:

Pol:	a	b	c	d	e	f	g	h	i
pH:	1.13	1.51	2.03	2.52	7.0	7.36	9.08	9.51	11.96

zwitterionic species of the supporting electrolyte on the DME. At pH values 1.13, 2.03, and 2.52, the third wave observed may be attributed to the cathodic dissolution of Hg in the presence of As^{3-} in accordance with Eq. (1), as previously discussed by some authors [9].

$$3Hg + 2As^{3-} = Hg_3As_2 + 6e^- \qquad (1)$$

The maximum observed for the As(III) reduction in acidic medium at *pH* 2.52 may be explained by the electroreduction of protonated As-species.

Microcoulometric experiments performed at the limiting regions of the different waves obtained at *pH* values 1.13, 2.03, and 7.36 showed that six electrons participate in the overall reduction at *pH* 1.13, and 2.03, whereas three electrons are involved at *pH* 7.36.

The second arsenite wave and the wave due to cathodic dissolution of Hg at *pH* 1.13 were completely eliminated by addition of mercuric nitrate as shown in Fig. 2. This was substantiated by obtaining a polarogram of 0.5 m*M* As(III) in a buffer solution of *pH* 1.13. The normal waves were recorded. The solution was then made ca. 0.04 m*M* of mercuric nitrate and the polarogram was immediately rerun. Complete elimination of the second arsenite wave was observed at the concentration of 0.48 m*M* mercuric nitrate. The three wave pattern is replaced by a single well developed wave shifted to a more negative potential. This behaviour confirms the interaction of free mercury ions with intermediate arsenite reduction products in the diffusion layer at *pH* 1.13. The disappearance of the second and third wave at *pH* 1.13 upon addition of mercuric nitrate may be attributed to the formation of

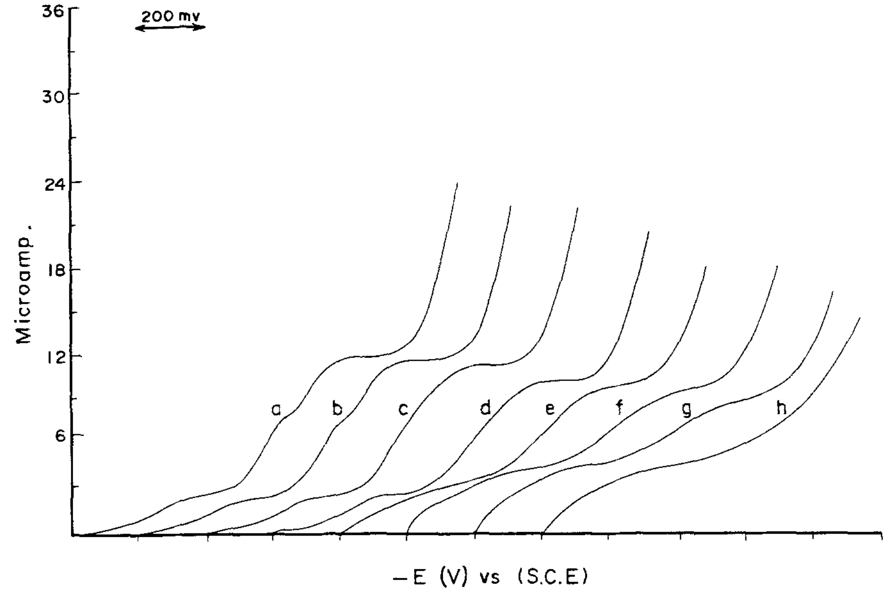

Fig. 2. Polarograms of (a) 0.5 m*M* As(III) in bicine buffer (*pH* 1.13) in presence of mercuric nitrate; (b) 0.04 m*M*; (c) 0.08 m*M*; (d) 0.160 m*M*; (e) 0.24 m*M*; (f) 0.32 m*M*; (g) 0.40 m*M*; (h) 0.48 m*M*. Each curve starts at −0.20 V

relatively insoluble Hg_3As_2 due to the interaction between the deposited arsenic, formed at the electrode surface, and the free mercury ions.

Coulometric reduction of 1.5 m*M* As(III) in bicine buffer solutions of *pH* values 1.13 and 2.03 was established with a large mercury cathode whose potential was maintained at −0.82 V and −1.65 V *vs.* S.C.E., respectively, by an automatic potentiostat. The reduction product produced a yellow-brown spot [21] by the interaction with a paper impregnated with mercuric bromide due to the formation of $H(HgBr)_2As$, $(HgBr)_3As$, and Hg_3As_2. This evidenced the formation of arsine.

In neutral solutions, As(III) does not produce anodic waves. Making the solution basic (*pH* 8.50) causes an anodic wave to appear. Gradual increase in the limiting current of this wave has been observed with increasing *pH*. At *pH* 11.96, an anodic wave appears and the cathodic wave disappears. If As(III) is present as AsO_2^- ions (free or complexed with N,N-Bis(2-hydroxyethyl)glycine ligand) at *pH* 8.5–9.0, the anodic dissolution of Hg would take place following Eq. (2)

$$Hg + 2AsO_2^- = Hg(AsO_2)_2 + 2e^-. \tag{2}$$

In a strongly alkaline medium (at $pH > 11$), reaction according to Eq. (3) can take place.

$$3Hg + 2AsO_3^{3-} \rightarrow Hg_3(AsO_3)_2 + 6e^-. \tag{3}$$

The anodic wave represented by Eq. (2) is lower than that of Eq. (3). This confirms the transformation of AsO_2^- ions, which are the electroreducible species, to AsO_3^{3-} ions in this medium. These ions were not reduced at the DME [12]. The disappearance of the cathodic wave of As(III) at *pH* 11.96 is an evidence for this

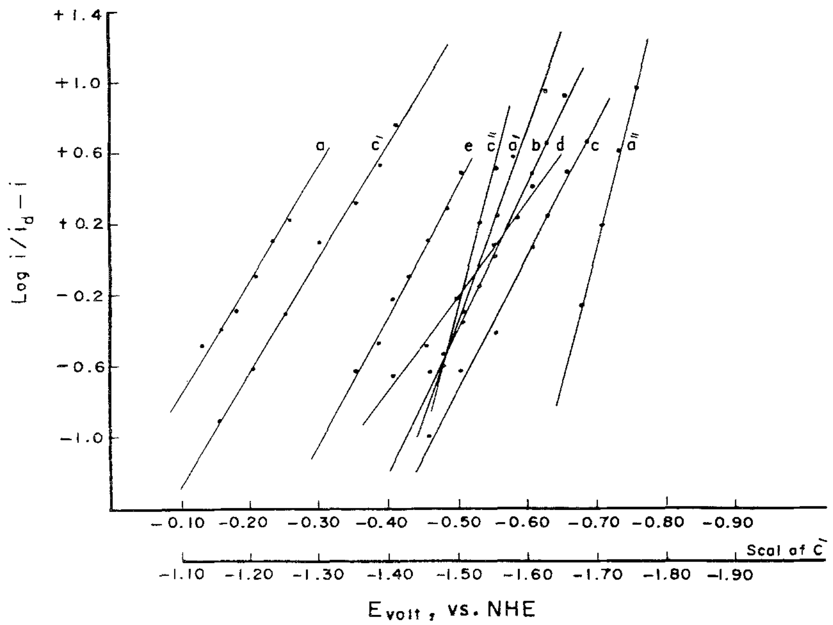

Fig. 3. Analysis of waves of 5×10^{-4} *M* As(III) in bicine buffer solutions:

Plot: a	$\bar{a}$	$\bar{\bar{a}}$	b	C	$\bar{C}$	$\bar{\bar{C}}$	d	e
Wave: 1st	2nd	3rd	main	1st	2nd	3rd	main	main
pH:	1.13		1.51		2.03		7.36	9.51

transformation. The behaviour at *pH* 9.51 can be considered as an intermediate step to complete transition of AsO_2^- to AsO_3^{3-}.

Nature of Reduction

The reduction of As(III) in bicine buffer solution was irreversible, judging from the logarithmic plot of the wave analysis, which was obtained by means of the plot of the values of log $i/(i_d - i)$ *vs.* E as shown in Fig. 3. These plots were utilized in the evaluation of the corresponding values of the kinetic parameters [22] and wave characteristics including slope, αn_a (α = transfer coefficient; n_a = number of electrons involved in the rate determining step), K° (standard rate constant), ΔG^* (energy of activation), and $KD^{-1/2}$. Table 1 summarizes the kinetic parameters, wave characteristics and microcoulometric data for the reduction of As(III) in bicine buffer solutions. These results, coupled with the values of the slopes of $\log i_l - \log h$ plots, as indicated in Table 1, show that the reduction of As(III) in bicine buffer solutions is irreversible and controlled by diffusion with the development of a slight adsorption component.

Differential Pulse Polarographic investigations

DPP investigation of a 0.01 *M* bicine buffer solution shows a good base line in the investigated potential range (0.0 to −1.20 V *vs.* Ag/AgCl·$KCl_{(s)}$) in the *pH* range 1–10. DPP behaviour of different concentrations of As(III) in 0.01 *M* bicine buffer solutions of *pH* 1.41 and 9.12 is represented by the polarograms shown in Figs. 4

Table 1. Kinetic parameters and microcoulometric data of the electroreduction of 5×10^{-4} *M* As(III) in bicine buffer solutions

pH	Wave	i_d (μA)	$E_{1/2}$(V) NHE	Slope (volt^{-1})	αn_a	$K°$ (cm/s)	ΔG^* (KJ)	$K°D^{-1/2}$	aS^*	D^* (cm^2 s^{-1})	Microcoulometry	
											E vs. SCE	*n*
1.13	1st	2.70	−0.158	5.33	0.319	6.27×10^{-4}	200.58	0.383	0.42		–	–
	2nd	5.70	−0.538	11.00	0.660	1.59×10^{-4}	215.01	0.098	0.73	2.685×10^{-6}	−0.82	5.766
	3rd	3.00	−0.698	16.00	0.960	–					–	–
1.51	main	8.10	−0.558	8.0	0.480	1.94×10^{-4}	212.87	0.123	0.57	2.49×10^{-6}	–	–
2.03	1st	6.6	−0.608	7.62	0.460	8.01×10^{-4}	197.99	0.124	–		–	–
	2nd	26.4	−1.310	6.67	0.400	1.88×10^{-3}	189.08	0.291	0.33	4.15×10^{-5}	−1.65	5.694
	3rd	7.50	−1.510	13.33	0.799	–	–	–	0.18		–	–
7.36	main	9.90	−1.53	5.14	0.308	3.70×10^{-4}	206.11	0.191	0.27	3.74×10^{-6}	−1.9	2.872
9.51	main	4.80	−1.43	7.20	0.432	1.57×10^{-4}	215.10	0.168	0.80	8.77×10^{-7}	–	–

aS^* = slope of $\log i_l - \log h$ plot; D^* = diffusion coefficient

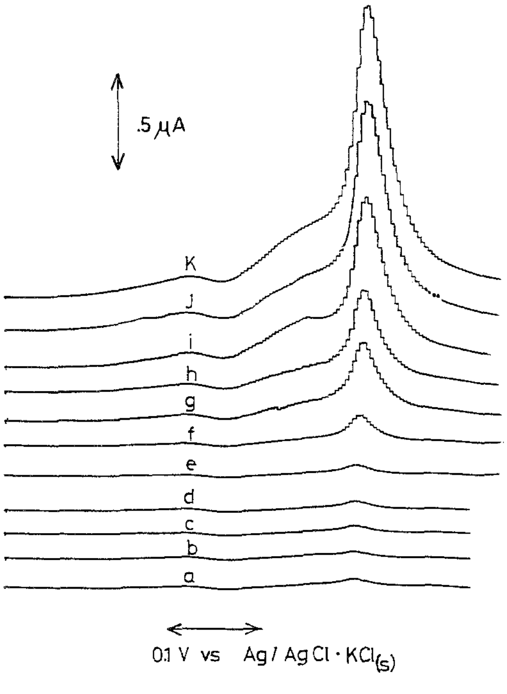

Fig. 4. Differential pulse polarography of different concentrations of As(III) in 0.01 *M* bicine buffer, *pH* 1.41, starting potential = −0.02 V *vs.* Ag/AgCl·$KCl_{(s)}$, drop time: 1 s, pulse amplitude = 50 mV, scan rate = 5 mV/S, As(III) concentrations: a 2×10^{-7} *M*, b 5×10^{-7} *M*, c 1×10^{-6} *M*, d 5×10^{-6} *M*, e 8×10^{-6} *M*, f 1×10^{-5} *M*, g 3×10^{-5} *M*, h 5×10^{-5} *M*, i 9×10^{-5} *M*, j 1.3×10^{-4} *M*, k 1.7×10^{-4} *M*

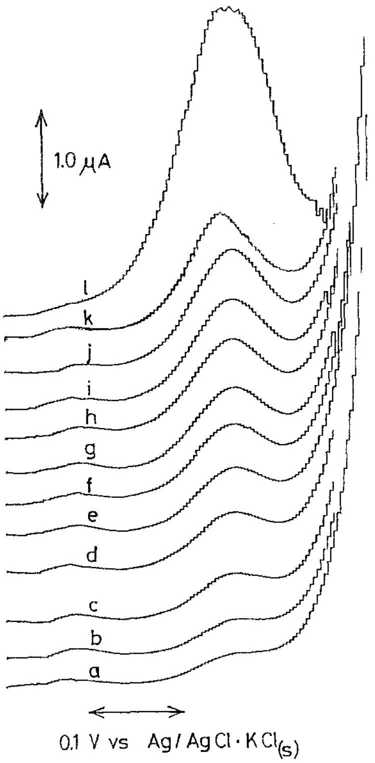

Fig. 5. Differential pulse polarography of different concentrations of As(III) in 0.01 *M* bicine buffer, *pH* 9.12, starting potential = −1.5 V *vs.* Ag/AgCl·$KCl_{(s)}$, other experimental parameters as in Fig. 4

and 5. At *pH* 1.41, the reduction peak observed at −0.56 V *vs.* Ag/AgCl·$KCl_{(s)}$ is suitable for the analytical determination of As(III). The half-peak width of this wave is 60 mV indicating an irreversible three electron reduction process. The calibration plots of these polarograms are listed in Table 2 with their linearity ranges, equations

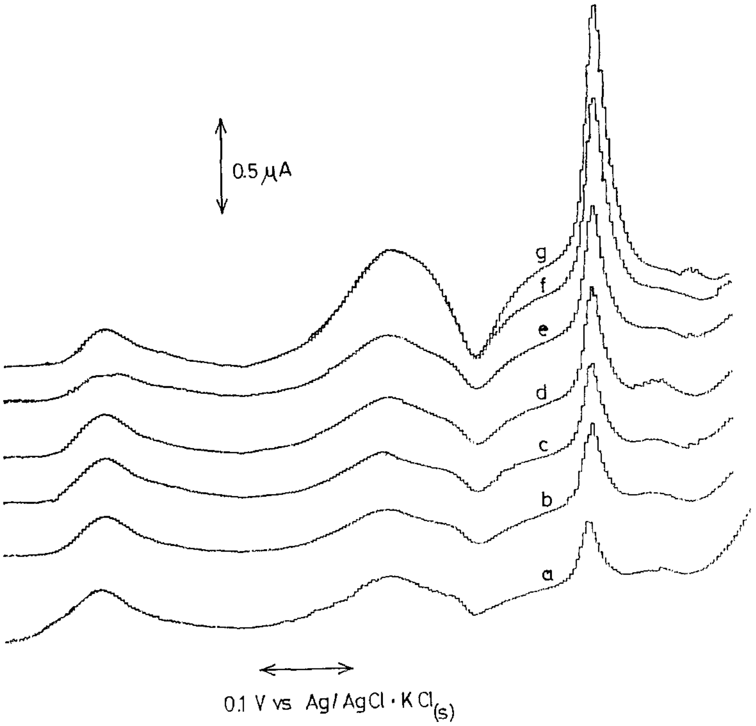

Fig. 6. Differential pulse polarography of different As(III) concentrations in the presence of 5×10^{-6} M of each Cu(II) and Se(IV), starting potential +0.1 V *vs.* Ag/AgCl·$KCl_{(s)}$, other parameters as in Fig. 4

and correlation coefficients. At *pH* 9.12, one reduction peak was observed at about −1.85 V *vs.* Ag/AgCl·$KCl_{(s)}$ with lower sensitivity than those obtained at strong acidic *pH* values. Moreover, these peaks have ill-defined morphology compared with those at strong acidic *pH* values. For these reasons, determination of As(III) in the presence of other interfering ions originally present in serum (*e.g.* Se(IV) and Cu(II)) has been investigated in strong acidic medium (bicine buffer solution of *pH* 1.41). Figure 6 shows the differential pulse polarograms of different As(III) concentrations in the presence of 5×10^{-6} M Cu(II) and 5×10^{-6} M Se(IV). The first reduction peak is due to Cu(II), the second and third peaks are due to Se(IV) and

Table 2. Characteristics of the calibration plots of As(III) in 0.01 M bicine buffer solution in absence and presence of Se(IV) and Cu(II) metal ions

Concentration range (M)	*pH*	Linearity range (M)	Regression line*	Correlation coefficient
2×10^{-7}–1.7×10^{-4}	1.41	1.7×10^{-4}	y = 0.127x + 0.2	0.9994
5×10^{-7}–3×10^{-5}	9.12	3×10^{-5}	y = 0.016x + 0.015	0.9992
2×10^{-7}–1.6×10^{-5}**	1.41	1.6×10^{-5}	y = 0.118x + 0.21	0.9986

* y in µA, x in 10^{-6} M, slope in µA/10^{-6} M, intercept in µA

** In the presence of 5×10^{-6} M Se(IV) and 5×10^{-6} M Cu(II)

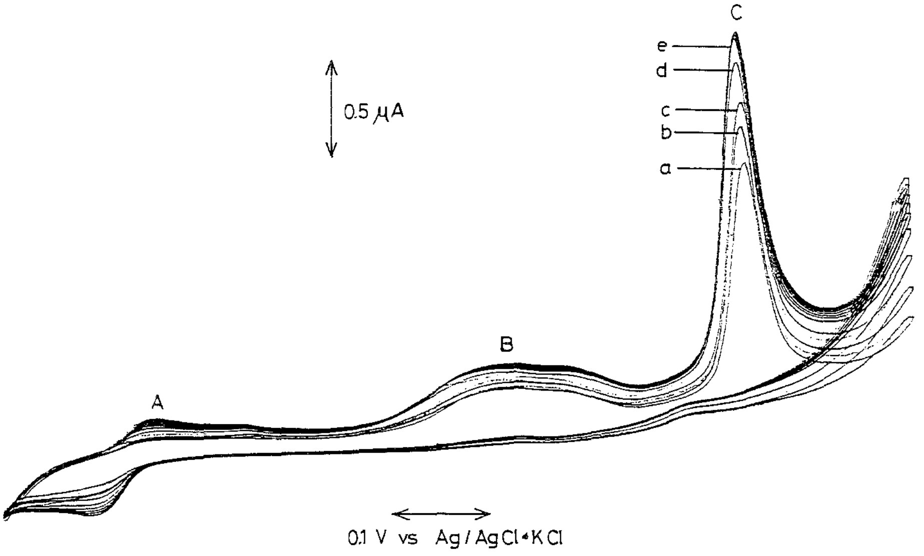

Fig. 7. Cyclic voltammograms of 5×10^{-6} *M* As(III) in presence of 5×10^{-6} *M* Cu(II) and 5×10^{-6} *M* Se(IV), 0.01 *M* bicine, *pH* 1.5, scan rate 100 mv/s, starting potential 0.0 V *vs.* Ag/AgCl·$KCl_{(s)}$; (A) Cu(II); (B) Se(IV); and (C) As(III), a first cycle, b second cycle, c third cycle, d fourth cycle and e fifth cycle

As(III), respectively. The regression lines of the calibration of As(III) are listed in Table 2.

Cyclic voltammetric investigations

The electrode reaction mechanism of As(III) in the presence of possible interfering metal ions, e.g. Cu(II) and Se(IV), is elucidated by running voltammograms of a ternary mixture of Cu(II), Se(IV), and As(III) (5×10^{-6} *M* for each ion). Both Se(IV) and As(III) gave irreversible reduction peaks as shown in Fig. 7 (B, C) while Cu(II) gave one reversible peak (A). It is obvious from the figure that the reduction of Se(IV) in presence of N,N-bis(2-hydroxyethyl)glycine takes place in two steps (part B of Fig. 7). It is worth mentioning that the As(III) voltammograms enhance when multiple cycles are applied on the same drop as indicated in the Fig. 7 by a, b, c, d and e.

The foregoing results concerning the voltammetric behaviour of arsenite ions AsO_2^- in aqeous zwitterionic buffer complexing electrolytes show that reduction of trivalent arsenic in these media at the DME takes place along one or three waves in accordance with one of the following schemes:

Scheme I

$$HAsO_2 + 3e^- + 3H^+ = As + 2H_2O \quad 1^{st}\text{ wave}$$

$$As + 3H^+ + 3e^- = H_3As \quad 2^{nd}\text{ wave}$$

$$3Hg + 2As^{3-} = Hg_3As_2 + 6e^- \quad 3^{rd}\text{ wave}$$

Scheme II

$$[AsO_2(L)_n]^- + 6e^- + 7H^+ = H_3As + 2H_2O + nL$$

Scheme III

$$[AsO_2(L)_n]^- + 3e^- + 2H_2O = As + 4OH^- + nL.$$

Here L refers to the N,N-Bis(2-hydroxyethyl)glycinate complexing ligand. Arsenious acid is a fairly weak acid ($pK_a = 9.18$ [19]), thus the meta arsenite ion AsO_2^- in bicine buffer solutions of pH values 1.13, 2.03, and 2.52 may give rise to the meta arsenious acid $HAsO_2$ which can be the electroreducible species and the reduction process takes place according to Scheme I. At pH 1.51, the reduction process takes place according to Scheme II. At a $pH \geqslant 7.0$, the electrode reaction involves liberation of OH^- ions, and reduction passes along a single wave as shown in Scheme III. It is worth mentioning that the polarographic reduction of arsenite ions at the DME in aqueous complexing media, *e.g.* bicine buffer solutions, depends on the pH of the solution. Separation of the reduction stages $As^{3+} + 3e^- = As$ and $As + 3e^- = As^{3-}$ is favoured at lower pH values. Thus, two intermingled waves are observed in a zwitterionic buffer solution of pH 1.13. This may be attributed to the fact that in aqueous solutions bicine gives rise to an equilibrium between its protonated and neutral forms and the N,N-Bis(2-hydroxyethyl)glycinate ion, governed by the acidity constants. In highly acidic solutions, only cations are present, and in highly alkaline solutions only anions. At intermediate pH values the majority of molecules is present in zwitterionic form. Thus different complexing species will predominate at different pH values which may lead to the previously observed polarographic behaviour of As(III) in bicine buffer solutions.

The differential pulse polarographic determination of As(III) is quite feasible and successful in bicine buffer solutions of pH 1.41 and 9.12. The regression lines for the calibration are shown in Table 2. The reproducibility of the method, expressed by the relative standard deviation of the current peak heights which were obtained from ten repeated determinations at pH 1.41, was 1.2%. The detection limit was $6.6 \times 10^{-8}\,M$ As(III) and $1.66 \times 10^{-7}\,M$ As(III) at pH values 1.41 and 9.12, respectively.

Interferences

In the presence of 0.01 M bicine buffer solution of pH 1.41, up to 100-fold Bi(III), Pb(II), Cd(II), Cu(II), Zn(II), V(V), Cr(III), Fe(II), Fe(III), In(III), Mn(II), Al(III), Mo(VI), Ge(IV), Pd(II), and 50-fold Tl(I), Sn(IV), Nb(V), Ta(V), Se(IV), 1000-fold alkali metals, alkaline earth metals, SiO_3^{2-}, PO_4^{3-}, NO_3^-, NO_2^-, F^-, Br^- and I^- do not interfere in the DPP determination of As(III) recommended in this work.

References

[1] Kolthoff I. M., Belcher R. (1957) Volumetric Analysis, Vol. 3. Interscience, New York

[2] Wilson C. L., Wilson D. W. (eds) (1960) Comprehensive Analytical Chemistry, Vol. 1B. Elsevier, Amsterdam

[3] British Standards 1121, Part 38 (1967)

[4] Arnold J. P., Johnson R. M. (1969) Talanta **16**: 1191

[5] Kolthoff I. M., Probst R. L. (1949) Anal. Chem. **21**: 753

[6] Haight G. P. (1954) Anal. Chem. **26**: 593

[7] Vignoli L., Cristau B., Gouezo F. (1961) Chim. Anal. (Paris) **43**: 439

[8] Vignoli L., Cristau B., Gouezo F. (1962) Chim. Anal. (Paris) **44**: 3
[9] Henry F. T., Kirch T. O., Thorpe T. M. (1979) Anal. Chem. **51**: 215
[10] Myers D. J., Janet O. (1973) Anal. Chem. **45**: 267
[11] Arnold J. P., Johnson R. M. (1967) Chem. Ind. **38**: 1062
[12] Hagiwara K., Murase T. (1960) Bunseki Kagaku **14**: 757
[13] Whitnack G. C., Brophy R. G. (1969) Anal. Chim. Acta **48**: 123
[14] William R. H., Rogers L. B. (1960) J. Am. Chem. Soc. **82**: 802
[15] Geyer R., Geissler M. (1963) Z. Chem. **3**(7): 267
[16] Buldini P. L., Ferri D., Lanza P. (1980) Anal. Chim. Acta **113**(1): 171
[17] Hassan A., Azab H. A., Hassan, R. M. (1987) Bull. Soc. Chim. Fr. **1**: 63
[18] Azab H. A., Hassan A., El Shatoury S. A. (1989) Monatsh. Chem. **120**: 425
[19] Vogel A. I. (1968) Quantitative Inorganic Analysis, 3rd edn. Longmans, London, p. 385
[20] Perrin D. D., Dempsey B. (1974) Buffers for *pH* and Metal Ion Control. Chapman and Hall, London, p. 144
[21] Gutzeit L. (1960) Analyst **85**: 629
[22] Galus Z. (1976) Fundamental of electrochemical analysis. PWN, Polish Scientific Publishers, Warsaw, p. 224

Received July 7, 1993. Accepted July 28, 1993