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Polarographic Behaviour and Determination of As(III) in Aqueous Complexing Electrolytes

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Summary. The polarographic behaviour and determination of As(III) in aqueous complexing electrolytes viz. universal and citrate buffer solutions of *pH* varying from 2.20–12.0 and 1.5–4.96, respectively, have been investigated at $T = 25°C$. It was shown that reduction of As(III) takes place along one, two or three waves depending upon the *pH* value. Microcoulometric experiments have been performed at the limiting region of the different waves obtained at different *pH* values. Schemes for the mechanism of reduction occurring at the *DME* have been deduced. A method for analytical determination of As(III) on both the micro- and macro-scales in universal and citrate buffer solutions, respectively, in the presence of a trace of triton-x-100 is reported.

Keywords. Trivalent arsenic; Polarography; Aqueous complexing electrolytes.

Polarographisches Verhalten und Bestimmung von As(III) in wäßrigen komplexierenden Elektrolyten

Zusammenfassung. Das polarographische Verhalten und die Bestimmung von As(III) in wäßrigen komplexierenden Elektrolyten, nämlich Universal- bzw. Citratpuffer bei *pH* 2.20 – 12.0 bzw. 1.5 – 4.96 wurde bei $T = 25\,°C$ untersucht. Es wurde gezeigt, daß die Reduktion von As(III) über eine, zwei oder drei Wellen, abhängig vom *pH*-Wert, verläuft. In den je nach *pH* verschiedenen Grenzregionen der einzelnen Wellen wurden microcoulometrische Experimente durchgeführt. Dabei wurden Schemata für den Mechanismus der Reduktion an der tropfenden Quecksilberelektrode abgeleitet. Zusätzlich wird über eine Methode für die analytische Bestimmung von As(III) sowohl im Mikro- als auch Makromaßstab in Universal- und Citratpuffer in der Gegenwart von Spuren an Triton-x-100 berichtet.

Introduction

Determination of the content of arsenic in biological and industrial specimens have been considered adequate to assess the presence, amount, and behaviour of this element. Numerous titrimetric and polarographic methods have been cited in the literature [1–18]. 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 reduction of arsenite ions at DME in universal and citrate buffer solutions in continuation of our work on the polarographic reduction and determination of oxygenated anions [19–22] in aqueous solutions.

Experimental

All chemicals used were of BDH grade.

A stock $0.0145\,\text{mol}\,\text{l}^{-1}$ sodium arsenite solution was prepared by dissolving the required amount of the BDH grade $NaAsO_2$ in bidistilled water. The resulting solution was then standardized by the bromate method [23]. Solutions of lower concentrations were then prepared by accurate dilutions. Universal buffer solutions were prepared as recommended by Britton [24] by mixing the proper volumes of $0.2\,\text{mol}\,\text{l}^{-1}$ NaOH solution and an acidic mixture containing phosphoric, acetic and boric acids, each at a concentration of $0.04\,\text{mol}\,\text{l}^{-1}$. $NaH_2C_6H_5O_7$-HCl buffer solutions with *pH* 1.5–4.96 were prepared [25].

Polarographic measurements were carried out with a Tacussel PRG 3 apparatus equipped with three Tacussel RMO 6 electrodes and a thermostat cell. A saturated calomel electrode served as the reference electrode. The dropping mercury working electrode had the following characteristics: $m = 1.625\,\text{mg}\,\text{s}^{-1}$ and $t = 4.8\,\text{s}\,\text{drop}^{-1}$.

To determine As, dissolve 1 gm of the ore in 20 ml aqua regia ($HCl + HNO_3$), add 20 ml 1 : 1 H_2SO_4, heat until SO_3 vapors appear. Add 0.5 g hydrazine sulphate and evaporate. To the dried residue add 2–3 drops of 0.1 *N* H_2SO_4 then dissolve with 20 ml H_2O and filter. Dilute the filtrate with H_2O to 200 ml. Saturate 5 ml of this solution with $N_2H_4 \cdot H_2SO_4$ and heat. Add triton-x-100 to give a final concentration of $2.5 \cdot 10^{-4}\%$ and dilute to 25 ml with the supporting electrolyte (citrate buffer solution of *pH* 2.0). The solution must be deaerated by passage of purified argon before determination of As(III) polarographically. By use of a calibration curve concentration of As could be determined.

Results

Current Potential Curves

The polarographic behaviour of $0.5\,\text{m}\,\text{mol}\,\text{l}^{-1}$ sodium arsenite in universal buffer solutions of *pH* varying from 2.20 to 12.0 is represented by the polarograms shown in Fig. 1. Our study has been restricted to the reduction waves observed at *pH*'s which are shown in Fig. 2, after elimination of the maximum by the addition of the least amounts of maximum suppressor, triton x-100. The results show that the reduction of arsenite ions occurs along three steps in the *pH* range 2.20–3.0, where the first and second waves seems to be two intermingled waves. At *pH* 6.0 the arsenite reduction wave is masked by the hydrogen wave which immediately follows it. It has been claimed that polarographic reduction of As(III) does not occur in neutral solution [4]. But in the presence of weak acids (acetic, phosphoric) in the supporting electrolyte reduction occurs and a maximum appears on the polarogram. The maximum appears directly before the final hydrogen discharge at $-1.55\,\text{V}$. The polarograms obtained at *pH* ranges 4.10–4.90 and 8.0–11.0 consist of a single wave. At *pH* 2.20–3.0, the third wave observed may be attributed, as previously discussed by some authors [9], to the cathodic dissolution of Hg in the presence of As^{3-} in accordance with Eq. (1).

$$3\,Hg + 2\,As^{-3} = Hg_3As_2 + 6\,e\,. \tag{1}$$

The maximum observed for As(III) reduction in acidic medium at *pH* (2.20–3.0) may be explained by the electroreduction of protonated As-species.

Microcoulometric experiments performed at the limiting regions of the different waves obtained at *pH*'s 2.20, 4.10 and 9.0 showed that six electrons participate in the overall reduction at *pH*'s 2.20 and 4.10, three electrons at *pH* 9.0.

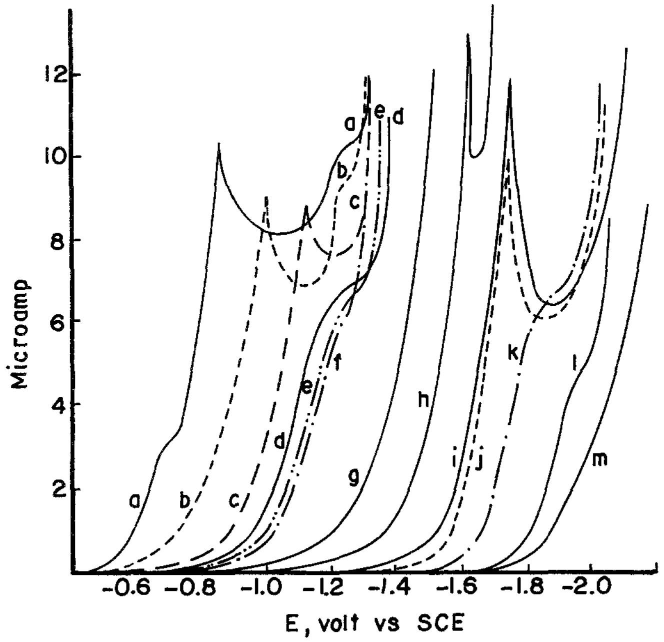

Fig. 1. Polarograms of 0.5 *mM* As(III) in universal buffer solutions

Curve:	a	b	c	d	e	f	g	h	i	j	k	l	m
pH:	2.2	3.0	4.1	4.5	4.9	5.0	6.0	7.0	8.0	9.0	9.9	11.0	12.0

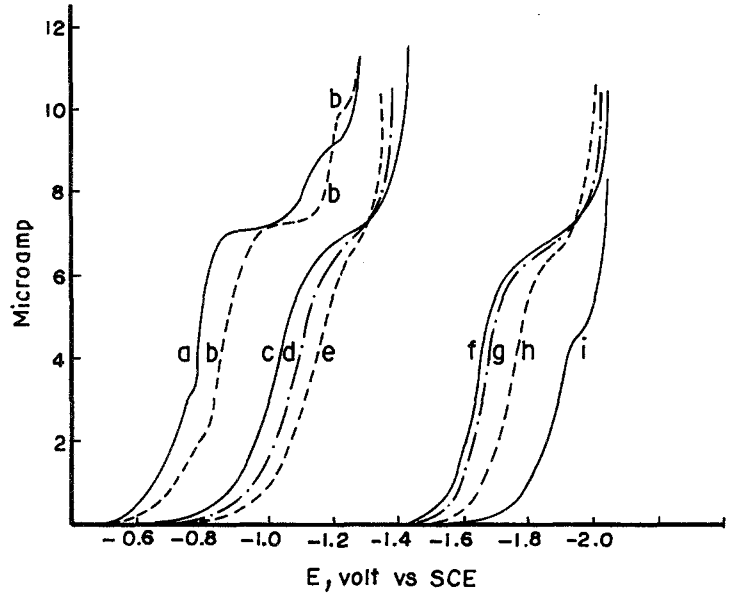

Fig. 2. Polarograms of 0.5 *mM* As(III) in universal buffer solutions in presence of T-x-100

Curve:	a	b	c	d	e	f	g	h	i
pH:	2.2	3.0	4.1	4.5	4.9	8.0	9.0	9.9	11.0
T-x-100%:	$1 \cdot 10^{-3}$	$5 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$	0.0	0.0	$1 \cdot 10^{-3}$	$5 \cdot 10^{-4}$	0.0	0.0

The second arsenite wave and the wave due to cathodic dissolution of Hg at *pH* 2.20 were completely eliminated by addition of mercuric nitrate as shown in

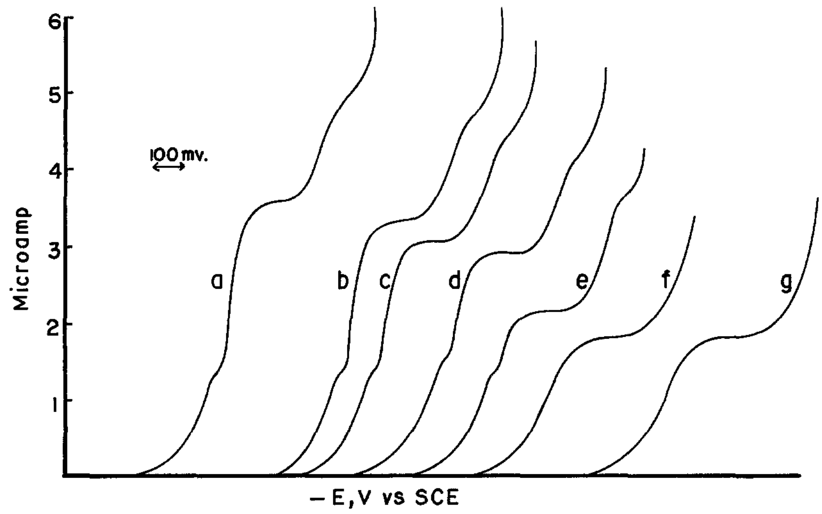

Fig. 3. Polarograms of (a) 0.2 *mM* As(III) + $1 \cdot 10^{-3}$% Triton-x-100 in universal buffer solution of *pH* 2.2 and in presence of mercuric nitrate; (b) 0.04 *m*M; (c) 0.08 *mM*; (d) 0.16 *mM*; (e) 0.24 *mM*; (f) 0.32 *mM*; (g) 0.4 *mM*. Each curve starts at − 0.4 *V*

Fig. 3. This was substantiated by obtaining a polarogram of 0.2 mmol l^{-1} As(III) in buffer solution of *pH* 2.20. The normal waves were recorded. The solution was then made ca. 0.04 mmol l^{-1} in mercuric nitrate and the polarogram was immediately rerun. The second arsenite wave was nearly eliminated. Complete elimination of the second arsenite wave was observed at the concentration of 0.32 mmol l^{-1} 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* 2.20. The disappearance of the second and third wave at *pH* 2.20 upon addition of mercuric nitrate may be attributed to the formation of 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 mmol l^{-1} solution As(III) in universal buffer solution of *pH*'s 2.20, 3.0 and 4.10 was established with a large mercury cathode whose potential was maintained at − 0.90 V, − 1.0 V and − 1.18 V vs. S.C.E., respectively, by an automatic potentiostat. The reduction product produced a yellow-brown spot [26] by the interaction with 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.

Anodic waves of As(III) obtained in universal buffer solutions of *pH* 8.5–12.0 are shown in Fig. 4. In neutral solutions, As(III) does not produce anodic waves. Making the solution basic (*pH* 8.5) causes an anodic wave to appear. Gradual increase in the limiting current of this wave has been observed with increasing *pH*. At *pH* 12.0 an anodic wave appears and the cathodic wave disappears. If As(III) is present as AsO_2^- ions (free or complexed with acetate ligand) at *pH* 8.5–9.0, the anodic dissolution of Hg would take place following Eq. (2).

$$Hg + 2\,AsO_2^- = Hg(AsO_2)_2 + 2\,e\,. \qquad (2)$$

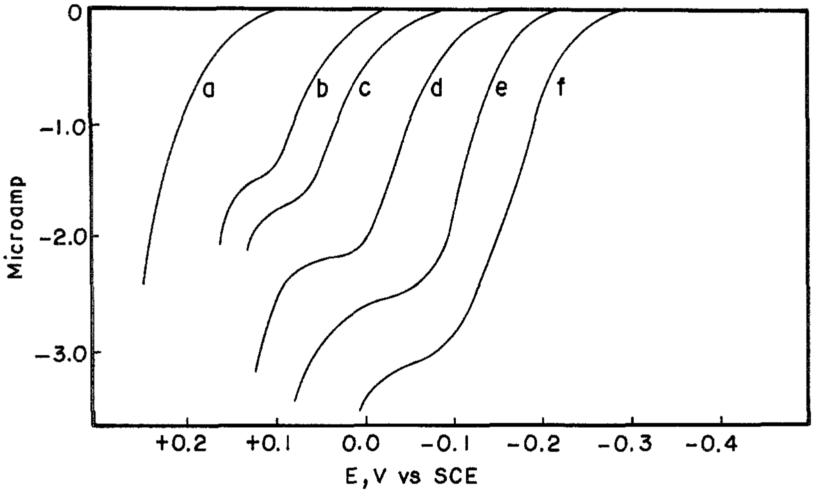

Fig. 4. Anodic waves of 0.5 *mM* As(III) in universal buffer solutions

Curve:	a	b	c	d	e	f
pH:	7.9	8.5	9.0	9.9	11.0	12.0
$E_{1/2}$:	–	+0.065	+0.025	−0.035	−0.115	−0.175

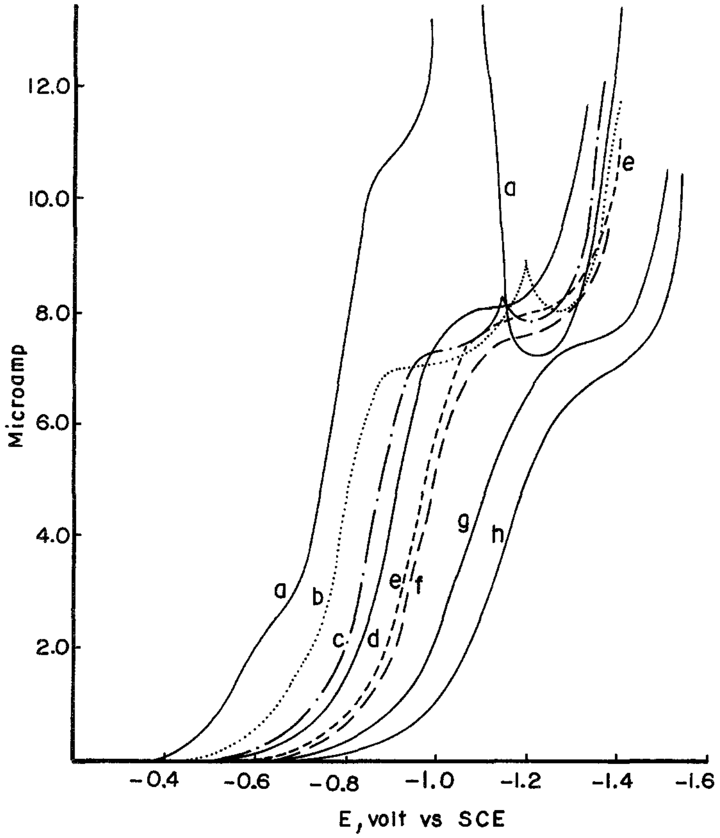

Fig. 5. Polarograms of 0.5 *mM* As(III) in citrate buffer solutions

Curve:	a	b	c	d	e	f	g	h
pH:	1.5	2.0	2.45	3.0	3.5	3.9	4.5	4.96

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

$$3\,Hg + 2\,AsO_3^{3-} \rightarrow Hg_3(AsO_2)_2 + 6\,e\,. \qquad (3)$$

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_2^{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* 12.0 is an evidence for this transformation. The behaviour at *pH* 11.0 can be considered as an intermediate step to complete transition of AsO_2^- to AsO_3^{3-}.

The polarographic behaviour of 0.5 mmol l^{-1} sodium arsenite in citrate buffer solutions of *pH* varying from 1.5 to 4.96 is represented by the polarograms shown in Fig. 5. Our study has been restricted to the reduction waves observed at *pH*'s shown in Fig. 6, after elimination of the maximum by the addition of the least amount of triton-x-100. The results show that reduction of As(III) occurs along three waves at *pH* 1.5, two waves at *pH* 2.0–2.45 and a single wave at *pH* 3.0–4.96. As the *pH* increases in both universal and citrate buffer solutions, the half wave potentials shifted to more negative values, indicating the formation of arsenic-acetate and arsenic-citrate complexes, respectively. The composition of the complex species probably depends on the conditions [4]. As shown in Fig. 6 the wave form in citrate buffer solutions is much better than in universal buffer solutions of

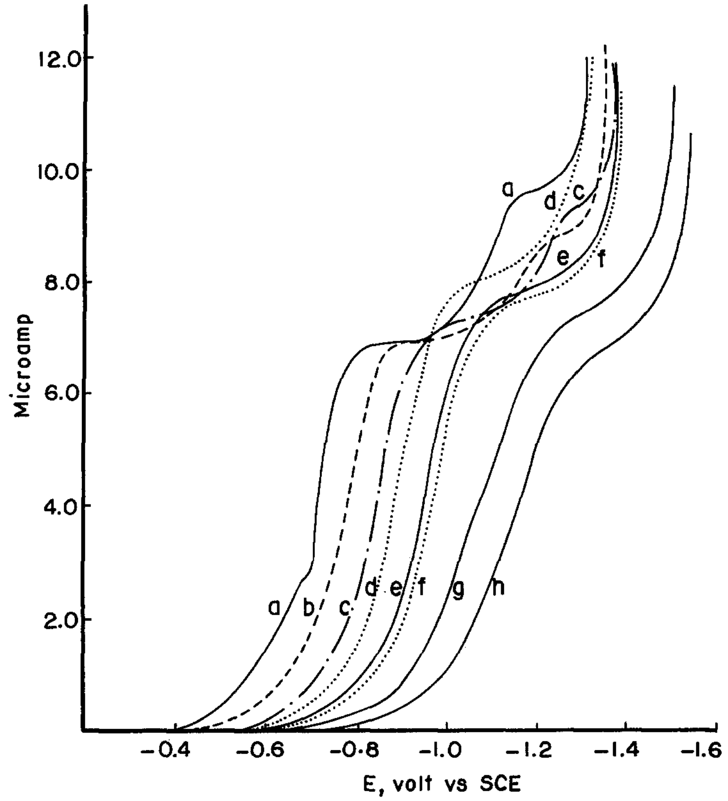

Fig. 6. Polarograms of 0.5 *mM* As(III) in citrate buffer solutions in presence of T-x-100

Curve:	a	b	c	d	e	f	g	h
pH:	1.5	2.0	2.45	3.0	3.5	3.9	4.5	4.96
T-x-100%:	$1\cdot10^{-3}$	$2.5\cdot10^{-4}$	$2.5\cdot10^{-4}$	0.0	0.0	0.0	0.0	0.0

pH 2.20–4.90. In view of the difficulty of obtaining satisfactory reduction waves with arsenic compounds these waves should be of considerable utility in practical analysis.

Microcoulometric experiments performed at the limiting region of the different waves obtained at pH's 2.0, 3.5 and 4.50 showed that six electrons participate in the electroreduction at the DME. The formation of arsine at the limiting region of the reduction waves obtained in citrate buffer solutions of pH's 2.0, 3.5 and 4.50 was confirmed by coulometric reduction of 1.5 mM solution of As(III) with a large mercury cathode whose potential was maintained at -0.95 V, -1.15 V and -1.30 V by an automatic potentiostat. The reduction product was identified as explained above.

Nature of Reduction

The reduction of As(III) in universal and citrate buffer solutions was irreversible, judging from the log-plot of the wave analysis, which was obtained by means of the plots of the values of $\log i/i_d - i$ vs. E. These plots were utilized in the evaluation of the corresponding values of the kinetic parameters and wave characteristics including slope, αn_a(α = transfer coefficient and n_a = number of electrons involved in the rate determining step), K^0 (standard rate constant), ΔG^* (energy of activation) and $KD^{-1/2}$. Tables 1 and 2 summarize the kinetic parameters, wave characteristics and microcoulometric data for the reduction of As(III) in both universal and citrate buffer solutions. These results coupled with the values of the slopes of $\log i_l - \log h$ plots, as indicated in Tables 1 and 2 show that the reduction of As(III) in both universal and citrate buffer solutions is irreversible and controlled by diffusion with the development of a slight adsorption component.

Effect of Concentration

The plots i_l vs. concentration for the different reduction waves of arsenite ions at different pH's in both universal and citrate buffer solutions are shown in Figs. 7 and 8. Deviation from linearity at higher depolarizer concentration was observed for the first one of the two intermingled waves and the total limiting current observed in universal buffer solution of pH 2.20. Accordingly, the reduction currents of these waves do not obey the Ilkovic equation except at a very narrow concentration range. The limiting currents of all other reduction waves are directly proportional to the concentration of As(III) indicating an accurate application for the Ilkovic equation. These results find support by constancy of the values of the current concentration coefficient shown in Tables 3 and 4. Fig. 9 illustrates the plots i_l vs. concentration for the different anodic waves of As(III) observed in universal buffer solutions of different pH's. Deviation from linearity at higher arsenite concentration was observed for the wave at pH 9.0. These plots indicate an accurate application of the Ilkovic equation in the pH range 9.9–12.0.

Table 1. Kinetic parameters and microcoulometric data for the reduction of 0.5 mmol l^{-1} As(III) in universal buffer solutions

pH	Wave	i_d μA	$E_{1/2}$, V NHE	Slope volt^{-1}	αn_a	$K°$ cm/s	ΔG^* kJ	$K° D^{-1/2}$	$S^{*,a}$	Microcoulometric data	
										E, vs. SCE	n
2.2	1st	3.10	−0.438	9.09	0.537	$2.84 \cdot 10^{-7}$	16.10	$1.10 \cdot 10^{-4}$	0.57	–	–
	2nd	4.04	−0.564	26.67	1.576	$2.49 \cdot 10^{-18}$	31.38	$9.61 \cdot 10^{-16}$		–	–
	3rd	2.22	−0.882	11.54	0.682	$1.81 \cdot 10^{-13}$	24.66	$7.01 \cdot 10^{-10}$		−0.90	5.890
3.0	1st	2.01	−0.484	12.50	0.699	$2.43 \cdot 10^{-9}$	18.96	$9.39 \cdot 10^{-7}$	0.55	–	–
	2nd	5.22	−0.840	16.45	0.910	$4.13 \cdot 10^{-7}$	92.70	$1.60 \cdot 10^{-14}$			
4.10	main	7.02	−0.764	8.96	0.530	$3.95 \cdot 10^{-10}$	20.05	$1.53 \cdot 10^{-7}$	0.48	−1.18	5.827
4.50	main	6.55	−0.824	7.47	0.438	$2.15 \cdot 10^{-9}$	19.03	$8.30 \cdot 10^{-7}$	0.60	–	–
8.00	main	6.63	−1.398	12.00	0.709	$4.57 \cdot 10^{-20}$	33.78	$1.76 \cdot 10^{-17}$	0.52	–	–
9.0	main	6.70	−1.416	10.00	0.591	$1.89 \cdot 10^{-17}$	30.17	$7.29 \cdot 10^{-15}$	0.57	−1.80	2.882
9.90	main	6.40	−1.484	9.40	0.556	$3.06 \cdot 10^{-17}$	29.88	$1.18 \cdot 10^{-14}$	0.48	–	–
11.0	main	4.70	−1.618	10.80	0.638	$9.15 \cdot 10^{-21}$	34.75	$3.53 \cdot 10^{-18}$	0.49	–	–

[a] S^* = slope of the log i_e – log h plot

Table 2. Kinetic parameter and microcoulometric data for the reduction of 0.5 mmol l^{-1} As(III) in citrate buffer solutions

pH	Wave	i_d μA	$E_{1/2}$, V NHE	Slope volt^{-1}	αn_a	$K°$ cm/s	ΔG^* kJ	$K° D^{-1/2}$	$S^{*,a}$	Microcoulometric data	
										E, vs. SCE	n
1.50	1st	2.66	−0.349	9.33	0.55	$1.51 \cdot 10^{-6}$	15.10	$5.83 \cdot 10^{-4}$	0.67	–	–
	2nd	2.75	−0.505	20.00	1.18	$2.17 \cdot 10^{-13}$	24.55	$8.37 \cdot 10^{-11}$	0.49		
	3rd	2.80	−0.831	10.00	0.59	$1.34 \cdot 10^{-11}$	22.08	$5.16 \cdot 10^{-9}$	–		
2.00	1st	7.23	−0.543	16.00	0.95	$5.59 \cdot 10^{-12}$	22.60	$2.16 \cdot 10^{-9}$	0.8	–	–
	2nd	1.80	−0.928	13.33	0.79	$1.16 \cdot 10^{-15}$	27.70	$4.46 \cdot 10^{-13}$		−0.95	5.867
2.50	1st	7.33	−0.578	8.88	0.53	$1.99 \cdot 10^{-8}$	17.69	$7.67 \cdot 10^{-6}$	0.8	–	–
	2nd	1.74	−0.968	20.00	1.18	$1.19 \cdot 10^{-22}$	37.36	$4.6 \cdot 10^{-20}$			
3.00	main	8.00	−0.638	8.57	0.51	$9.28 \cdot 10^{-9}$	18.15	$3.58 \cdot 10^{-6}$	0.8	–	–
3.50	main	7.60	−0.688	8.00	0.47	$8.54 \cdot 10^{-9}$	18.20	$3.30 \cdot 10^{-6}$	0.48	−1.15	5.851
3.90	main	7.65	−0.708	8.00	0.47	$5.91 \cdot 10^{-9}$	18.42	$2.28 \cdot 10^{-6}$	0.48	–	–
4.50	main	7.40	−0.810	5.88	0.35	$4.7 \cdot 10^{-8}$	17.18	$1.82 \cdot 10^{-5}$	0.46	−1.30	5.872
4.96	main	6.97	−0.885	6.40	0.38	$5.91 \cdot 10^{-9}$	18.42	$2.28 \cdot 10^{-6}$	0.48	–	–

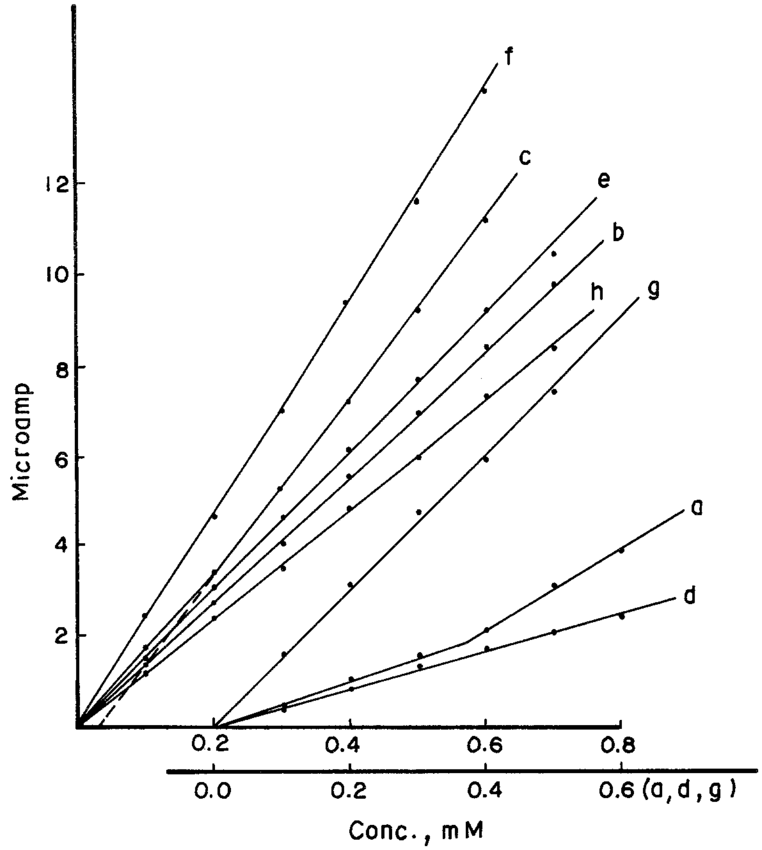

Fig. 7. Effect of As(III) concentration in universal buffer solutions

Plot:	a	b	c	d	e	f	g	h
pH:	2.2	2.2	2.2	3.0	3.0	3.0	4.1	4.5
$-E$, vs. SCE:	0.76	1.00	1.22	0.81	1.05	1.25	1.20	1.23

Discussion

The foregoing results concerning the polarographic behaviour of arsenite ions AsO_2^- in aqueous universal and citrate buffer solutions as complexing electrolytes show that reduction of trivalent arsenic in these media at the DME takes place along one, two or three waves in accordance with one of the following schemes:

Scheme I.

$$\begin{array}{lll} HAsO_2 + 3e + 3H^+ = As + 2H_2O & 1^{st}\text{ wave,} \\ As + 3H^+ + 3e = H_3As & 2^{nd}\text{ wave,} \\ 3Hg + 2As^{3-} = Hg_3As_2 + 6e & 3^{rd}\text{ wave.} \end{array}$$

Scheme II.

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

Scheme III.

$$[AsO_2(L)_n]^- + 3e + 2H_2O = As + 40H^- + nL.$$

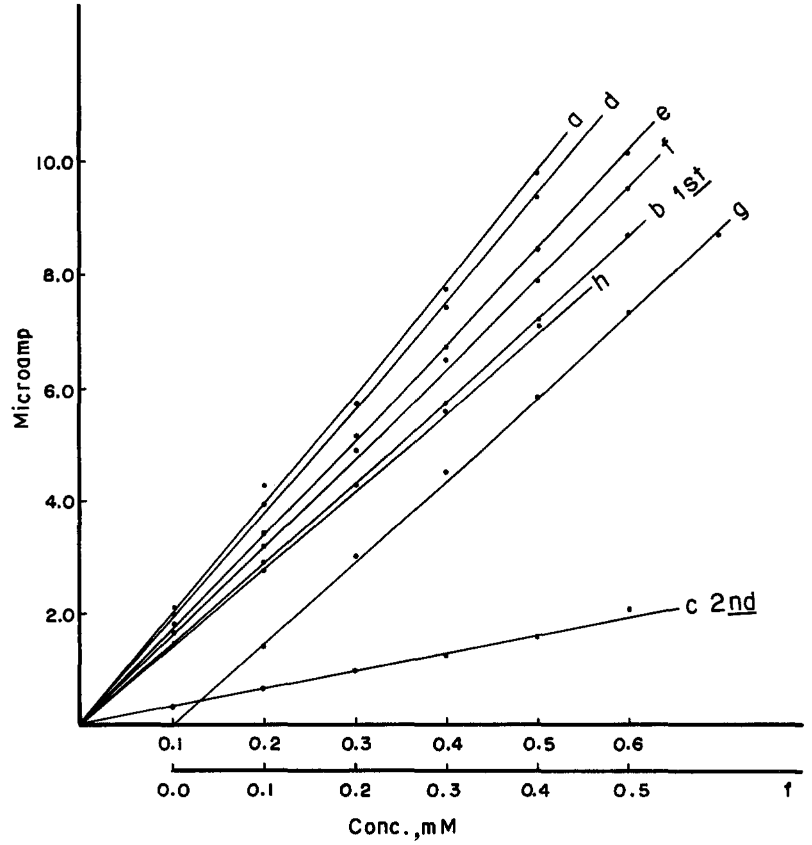

Fig. 8. Effect of As(III) concentration in citrate buffer solutions

Plot:	a	b	c	d	e	f	g	h
pH:	1.5	2.0	2.0	2.45	3.0	3.5	4.5	4.96
$-E$, vs. SCE:	1.2	0.96	1.22	1.25	1.1	1.2	1.3	1.35

Here L refers to the acetate or citrate complexing ligand. Arsenious acid is a fairly weak acid $pK_a = 9.18$ [23], thus the meta arsenite ion AsO_2^- in universal buffer solutions of *pH* 2.20–3.0 and citrate buffer solution of *pH* 1.50 may give rise to the meta arsenious acid $HAsO_2$ which can be considered as the electroreducable species and the reduction process takes place according to Scheme I. In weakly acid solutions (universal buffer of *pH* 4.10–4.90) where the arsenic-acetate complexes are the electroreducable species, the reduction process takes place according to Scheme II. The same scheme may be held for the first wave at *pH* 2.0–2.45 and the main wave at *pH* 3.0–4.96 citrate buffer solutions. At higher *pH's* > 7.0 the electrode reaction involves liberation of OH^- ions, and reduction passes along a single wave as shown in Scheme III. It is worthy to mention that the polarographic reduction of arsenite ions at the DME in aqueous complexing media viz. universal and citrate 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 at these *pH* values.

The polarographic determination of arsenious acid is quite feasible and successful on both the micro- and macro scales in universal buffer solutions of *pH* 2.20–

Table 3. Effect of As(III) concentration in universal buffer solution of *pH*4.10 at − 1.20 volt vs. SCE

C (mmol l^{-1})	$i_{d\,(\mu A)}$	$i_{d/c}$	Average
0.10	1.56	15.60	15.50
0.20	3.13	15.70	
0.30	4.67	15.60	
0.40	5.92	14.80	
0.50	7.43	14.90	
0.60	9.40	15.80	
0.70	11.12	15.90	

Table 4. Effect of As(III) concentration in citrate buffer solution of *pH*3.0 at − 1.10 volt vs. SCE

C (mmol l^{-1})	$i_{d\,(\mu A)}$	$i_{d/c}$	Average
0.10	1.76	17.59	17.03
0.20	3.43	17.17	
0.30	5.18	17.26	
0.40	6.68	16.70	
0.50	8.35	16.71	
0.60	10.04	16.74	

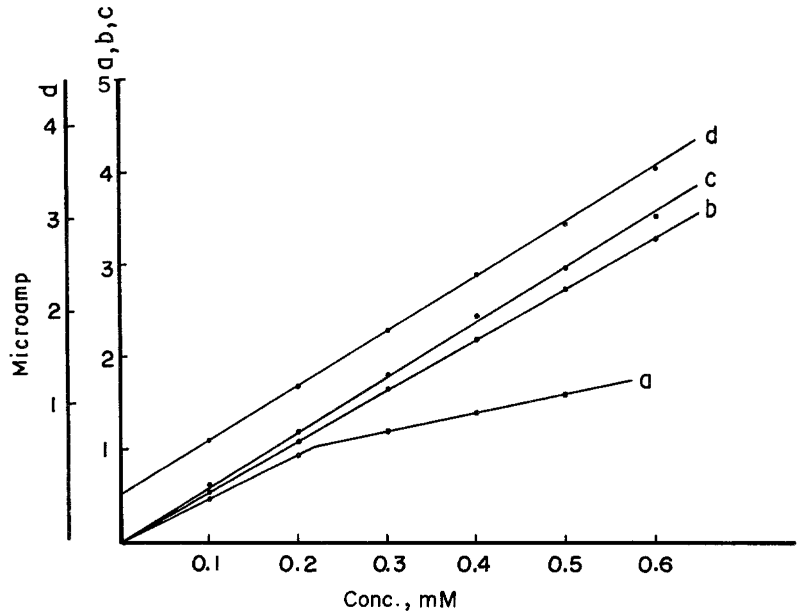

Fig. 9. Effect of [As(III)] on the limiting current of the anodic waves in universal buffer solutions

Plot:	a	b	c	d
pH:	9.0	9.9	11.0	12.0
E, vs. SCE:	+0.08	+0.04	−0.01	−0.08

4.90, using cathodic reduction of As(III) and in *pH* 9.0–12.0 using anodic oxidation of As(III) to As(V). In the latter case, no interference was found from bismuth, lead, cadmium, zinc, vanadium, tungsten, chromium, calcium, barium, potassium, sodium, tin(IV), antimony(III), carbonate, sulphate or phosphate. Polarographic determination of As(III) within the range 7.49 μg/ml to 0.05 mg/ml in universal buffer solutions (*pH* 2.20–4.50 and *pH* 9.0–12.0) and within the range 7.49 μg/ml to 0.045 mg/ml in citrate buffer solutions (*pH* 1.5–4.96) is successful. This was confirmed by the calibration curves shown in Figs. 7, 8, and 9.

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