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POLAROGRAPHIC INVESTIGATION OF THE SYSTEMS ARSENIC(III)-TARTARIC ACID AND ARSENIC(III)-1,2-DIAMINO-CYCLOHEXANE-N,N,N',N'-TETRAACETIC ACID (DCTA)

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POLAROGRAPHIC INVESTIGATION OF THE SYSTEMS ARSENIC(III)-TARTARIC ACID AND ARSENIC(III)-1,2-DIAMINO- CYCLOHEXANE-N,N,N',N'-TETRAACETIC ACID (DCTA)

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SUMMARY

The reactions between As(III), tartaric acid (H_2T) and DCTA were investigated polarographically. The conditional stability constants of As(III)-complexes at a given pH-value and variable ligand concentration were calculated from the change of the limiting currents. The optimum conditions for calculating stability constants from the current were also discussed. It was found that DCTA (H_4L) formed the complex $[As(OH)_2HL]^{2-}$ whose overall formation constant was $lg\beta_{111} = (20.67 \pm 0.09)$ at $\mu = 0.1$ and $t^\circ = (25.0 \pm 0.2)^\circ C$, whereas the complex between As(III) and H_2T was $[As(OH)_2T]^-$ with an overall stability constant $lg\beta_{101} = 6.62 \pm 0.14$ at $\mu = 0.1$ and $t^\circ = (25 \pm 0.2)^\circ C$.

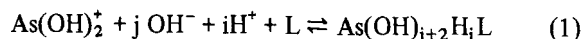
In earlier systematic investigations¹⁻⁴ of the effect of some organic acids on the polarographic behaviour of As(III) we showed that the acids not only provided protons consumed by the electrode reaction, but also formed complex compounds with arsenite. The present paper describes further investigations on the complexation between As(III) and 1,2-diamino-cyclohexane-N,N,N',N'-tetraacetic acid (DCTA), as well as between As(III) and tartaric acid (H_2T). Arsenic (III) is known to react with H_2T to yield a 1 : 1 complex, but there are no data about the formula and the stability constant of this compound⁵⁻⁷. The reaction of As(III) with DCTA has not yet been investigated in detail, although formation constants for many metal-DCTA complexes have been reported⁸. Only polarographic half-wave potentials of the As(III)-wave in the presence of DCTA in various media are mentioned in the literature⁹.

We have previously developed a technique for calculating stability constants based on the As(III)-diffusion currents obtained in the absence and

the presence of a ligand¹⁻⁴. We now wish to demonstrate also the importance of choosing the right optimum conditions in order to obtain correct values of the stability constants with this technique.

THEORETICAL

Consider that the complex formation between As(III) and the fully dissociated acids (H_2T or DCTA) takes place according to the reaction:



The overall formation constant is:

$$\beta = \frac{[As(OH)_{j+2}H_iL]}{K_w^j [H^+]^{i-j} [L] [As(OH)_2^+]} = \frac{\beta' \cdot \alpha_{As(OH)_2} \cdot \alpha_{LH}}{K_w^j \cdot [H^+]^{i-j}} \quad (2)$$

where β' is the conditional stability constant, $\alpha_{As(OH)_2}$ – the coefficient for the side reaction of $As(OH)_2^+$ with OH^- , α_{LH} – that for the reaction between acid anion, L, and protons, and K_w is the ion-product of water.

In the calculation of the conditional stability constant

$$\beta' = \frac{[As(OH)_{j+2}H_iL]}{C'_{As} \cdot C'_L} = \frac{\bar{i} - \bar{i}_o}{(\bar{i}_{As} - \bar{i} + \bar{i}_o) \cdot C'_L} = \frac{\alpha_1}{(1 - \alpha_1)C'_L} \quad (3)$$

C'_{As} , C'_L are the free concentrations of the corresponding species, \bar{i} – the diffusion current at a given ligand concentration, \bar{i}_o – the limiting diffusion current in the absence of ligand, and \bar{i}_{As} – the limiting current with complete complexation, found

when an appropriate excess of the ligand is present in the solution, α_1 is the fraction of the complex, equal $\bar{i} - \bar{i}_0 / \bar{i}_{As}$. This relation between β' and the currents is valid when reaction (1) is so inert that the complex $As(OH)_{j+2}H_jL$ is the only reducible on the mercury dropping electrode, hence the limiting current, \bar{i} , is diffusion controlled and proportional to the complex concentration¹⁰.

It can be shown that the maximum relative error in β' is given by

$$\frac{\Delta\beta_1}{\beta_1} = \pm \frac{\Delta\alpha_1}{\alpha_1(1 - \alpha_1)} \quad (4)$$

In the latter equation the maximum relative error in α_1 is connected with the measured currents as follows

$$\frac{\Delta\beta_1}{\beta_1} = \pm \left(\frac{\Delta\bar{i}}{\bar{i} - \bar{i}_0} + \frac{\Delta\bar{i}}{\bar{i}_{As}} \right) \quad (5)$$

According to eqns 4 and 5 the error in β' will obviously depend on the relative error in α_1 , as well as on the $(1 - \alpha_1)$ - values. The optimum condition, connected with a minimum error in β' is $\alpha_1 = \frac{1}{2}$, e.g. $\bar{i} - \bar{i}_0 = 1/2 \bar{i}_{As}$. This condition is not satisfied for weak complexes, since in these cases $\bar{i} - \bar{i}_0 < \bar{i}_{As}$, so that relative small errors in α_1 will appreciably affect the values of the conditional stability constants. Better results in β' may be obtained for these systems when some other method, such as the extrapolation method is used¹¹. In the present study we employed a method based on an idea proposed by Jatzimirzkii¹¹. The following general equations were adopted

$$f_1 = \frac{\bar{i} - \bar{i}_0}{C_{As} \cdot C_L} = \frac{\mathcal{K}_1 \beta' [L]}{\{1 + \beta' [L]\} C_L} \quad (6)$$

$$f'_1 = f_1 \cdot C_L \quad (7)$$

In these equations \mathcal{K}_1 is the Ilkovic constant, and C_{As} and C_L are the analytical concentrations of As and L. Should the free ligand concentration, $[L]$, differ from C_L , an iterative procedure must be adopted¹² repeating the calculations until two consecutive values of β' are satisfactorily constant. We are now showing, however, that the extrapolated functions are given by eqns 8 and 9.

$$\lim_{C_L \rightarrow 0} f_1 = \frac{\mathcal{K}_1 \beta'}{1 + \beta' C_{As}} = \mathcal{K}_1 \quad (8)$$

$$\lim_{C_L \rightarrow 0} f'_1 = \mathcal{K}_1 \quad (9)$$

The required value of β' may, therefore, be obtained from the relation 10 without using an iterative procedure.

$$\beta' = \frac{\mathcal{A}_1 / \mathcal{K}_1}{1 - \mathcal{A}_1 / \mathcal{K}_1 \cdot C_{As}} = \frac{x}{1 - x C_{As}} \quad (10)$$

Equation (10) can be used for the calculation of β' from the extrapolated values of \mathcal{A}_1 and \mathcal{K}_1 , as well as for developing a criterion for the feasibility of this extrapolation procedure. Evidently, when $\mathcal{A}_1 / \mathcal{K}_1 \cdot C_{As} \ll 1$, the free ligand concentration is equal to the total concentration, so that no iteration is necessary.

The maximum relative error in β' calculated by using eqn (10) is given by eqn (11).

$$\delta\beta' = \pm \frac{\Delta x}{x(1 - x C_{As})} \quad (11)$$

The optimum conditions in determining β' connected with the minimum of the function $\beta'(x)$ exists when $\mathcal{A}_1 / \mathcal{K}_1 \leq 1/2 C_{As}^{-1}$. If this condition is not satisfied, the error in β increases to such an extent that the data obtained by this technique must be treated with the greatest caution. When $\mathcal{A}_1 / \mathcal{K}_1 \cdot C_{As} \approx 1$, small errors in $\mathcal{A}_1 / \mathcal{K}_1$ will give rise to such large errors in β' so that data in this range must be discarded.

The function (8) and (9) can also be used to predict the limits in which the two parameters \mathcal{K}_1 and β_1 are to be determined. If the complex is weak enough, so that $1 > \beta' [L]$ and $1 > \beta' \cdot C_{As}$, it is not the required values of β' that are found, but the product $\mathcal{K}_1 \beta'$.

EXPERIMENTAL

All reagents were of analytical grade. Stock solutions of arsenite were prepared by dissolving a known amount of As_2O_3 in redistilled water and standardizing the solutions by the bromatometric method¹³. The tartaric acid ('Reachim', USSR, p.a) solutions were prepared fresh daily. The stock solution of DCTA (produced by 'Reanal' - Hungary, p.a.) was prepared by dissolving its disodium salt in redistilled water. All pH adjustments were made with sulfuric acid or sodium hydroxide and the pH-values were measured with a Seibold-GV-52 pH-meter. The ionic strength was adjusted to 0.1 with Na_2SO_4 . All polarographic curves were recorded by a Czechoslovak LP-60 polarograph, with a sensitivity of

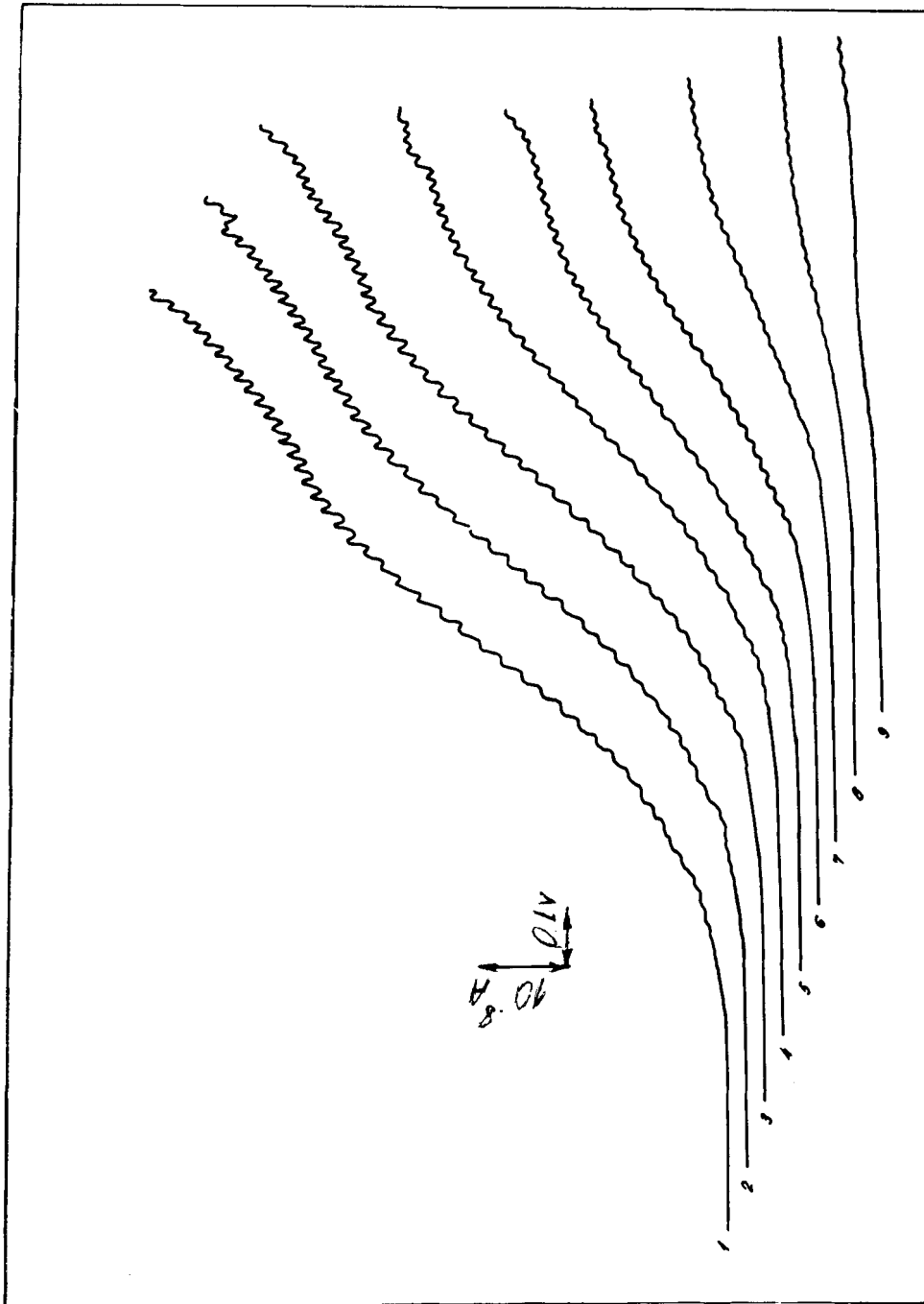


FIGURE 1 DC-Current voltage curves of the As(III)-DCTA complex at pH 5.00 in solutions containing $6.04 \cdot 10^{-4}$ M As(III) and varying $C_{DCTA} \cdot 10^3$ 1 - 9.0; 2 - 7.5; 3 - 6.0; 4 - 4.5; 5 - 3.0; 6 - 2.4; 7 - 1.5; 8 - 0.6; 9 - 0 recorded from -0.4 v (see); sensitivity - 1/150, for curve No. 9 - 1/7.

the galvanometer of $1.0 \cdot 10^{-3} \mu\text{A}/\text{div}$. The dropping mercury electrode used had a value of 1.23 mg/sec. and a drop time of 4.76 sec. in an air-free 0.1 M potassium chloride in short circuit. A salt bridge connected the external saturated calomel electrode with the polarographic cell and the system was thermostated at $25.0 \pm 0.2^\circ\text{C}$. The dissolved oxygen in the solution was expelled by passing nitrogen gas through the solution.

RESULTS AND DISCUSSIONS

All measurements showed that the polarographic waves of As(III) in presence of H_2T and DCTA were diffusion controlled (the limiting currents were proportional to the square root of the effective pressure of mercury and their temperature coefficients were about 2 per cent per 1°C). The electrode reaction was found to be irreversible, proved by the plots of $\lg \bar{i}/\bar{i}_d - \bar{i}$ vs $E^{1.4}$. From all these measurements it follows that As(III) forms electroactive complexes with H_2T and DCTA so inert that their stability constants may be found from the currents, using the above calculation techniques.

As(III) – DCTA System

Fig. 1 shows the current–voltage curves of As(III) at various DCTA-concentrations. The half-wave potential shifts to more negative values and indicates formation of a complex. The limiting current is a function of the ligand concentration. Preliminary investigations with different DCTA and As(III) concentrations showed that the current was proportional to the complex concentration and constant, when the complexation was complete, as can also be seen in Fig. 2. The limiting currents of mixtures with fixed C_{As} ($2.0 - 6.0 \cdot 10^{-4}$ M As(III)) and pH and various ligand concentrations, $C_L : C_{\text{As}}$, from 0 to 25 were measured and these experiments were repeated at various pH-values between 4.0 and 6.5. At $\text{pH} < 4.0$ the current \bar{i}_o was too great, whereas at $\text{pH} > 6.0$ the equilibrium was unfavourable. To evaluate the conditional stability constant β' the limiting currents were measured for given C_{As} and different C_{DCTA} and the optimum measurement conditions for obtaining the best β' -values were chosen, according to eqns 4 and 5. Both calculation methods based on eqn. 3 and eqn. 10 are illustrated in Table 1, where the individual and mean values of the conditional stability constants are represented. The results clearly show that β' is

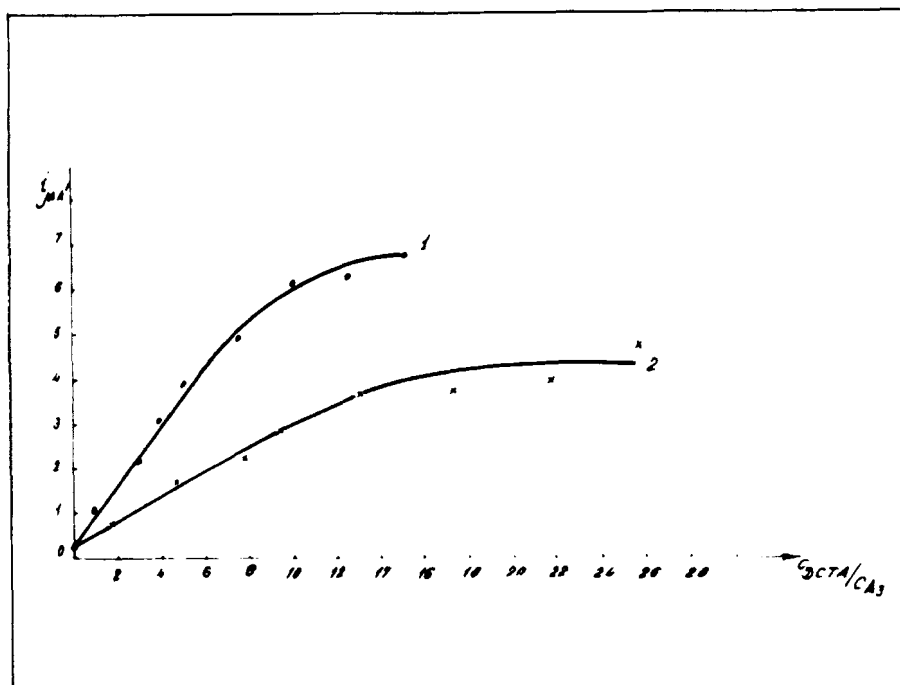


FIGURE 2 Relation between the limiting current and the ratio $C_{\text{DCTA}}/C_{\text{As}}$, obtained in 1 – $6.04 \cdot 10^{-4}$ M As(III) and 2 – $2.32 \cdot 10^{-4}$ M As(III)-solutions at pH 5.00.

TABLE I
Data for conditional stability constants obtained using eqn 3 (β^*) and using the extrapolation method (β')

$C_{As} = 2,32 \cdot 10^{-4}$ M; pH = 5.00; $\bar{i}_{As} = 4.11 \mu A$					
No	$C_{DCTA} \times 10^3$ M	\bar{i} μA	β^*	$f_1 \times 10^{-6}$	$f_2 \times 10^{-4}$
1	6.0	4.80		3.30	1.98
2	5.0	4.00		3.27	1.64
3	4.0	3.75		3.82	1.53
4	3.0	3.70		5.00	1.50
5	2.0*	2.90	$9,60 \cdot 10^2$	5.82	1.16
6	1.6*	2.30	$6,54 \cdot 10^2$	5.65	0.90
7	1.0*	1.70	$5,76 \cdot 10^2$	6.50	0.65
8	0.4	0.75		5.92	0.23
9	0	$\bar{i}_0 = 0.20$		—	—

$$\lg \beta^{-1*} = 2.86 \quad \begin{aligned} \mathcal{A}_1 &= 7,25 \cdot 10^6 \\ \mathcal{N}_1 &= 2,10 \cdot 10^4 \\ \lg \beta' &= 2.57 \end{aligned}$$

$C_{As} = 6,04 \cdot 10^{-4}$ M; pH = 5.00; $\bar{i}_{As} = 10,69 \mu A$					
No	$C_{DCTA} \times 10^3$ M	\bar{i} μA	β^*	$f_1 \times 10^{-6}$	$f_2 \times 10^{-4}$
1	9.0*	6.75	$1,75 \cdot 10^2$	1.20	1.08
2	7.5*	6.30	$1,76 \cdot 10^2$	1.34	1.00
3	6.0*	6.15	$2,08 \cdot 10^2$	1.64	0.98
4	4.5*	4.95	$1,77 \cdot 10^2$	1.74	0.78
5	3.0*	3.90	$1,76 \cdot 10^2$	2.04	0.61
6	2.4*	3.15	$1,58 \cdot 10^2$	2.03	0.49
7	1.5	2.18		2.16	0.32
8	0.6	1.05		2.32	0.14
9	0	$\bar{i}_0 = 0.21$		—	—

$$\lg \beta^{-1*} = 2.23 \quad \begin{aligned} \mathcal{A}_1 &= 2,35 \cdot 10^6 \\ \mathcal{N}_1 &= 1,22 \cdot 10^4 \\ \lg \beta^1 &= 2.34 \end{aligned}$$

constant at a given pH and \bar{i}_{As} and β' is independent of C_{As} and C_{DCTA} , which was confirmed statistically. Hence the conditional stability constant is independent of As(III) and DCTA-concentrations, which indicates conclusively that one type of 1 : 1 complex exists in solution. The values of $\alpha_{As(OH)_2}$ and $\alpha_{L(H)}$ were then calculated from the data given by ^{15,16}. The mean values of $\lg \beta' \cdot \alpha_{As(OH)_2} \cdot \alpha_{L(H)}$ (see Table 2) when plotted against pH gave a straight line with a slope equal to unity. The equations of both linear curves, calculated by the method of least squares, were:

$$\lg \beta' \cdot \alpha_{As} \cdot \alpha_L = 20.88 - 1.03 \text{ pH}$$

and

$$\lg \beta' \alpha_{As} \cdot \alpha_L = 20.57 - 0.99 \text{ pH}$$

TABLE II
Logarithmic values of the stability constants at different pH

pH	$\lg \beta'^*$	$\lg \beta'^* \alpha_{As} \alpha_L$	$\lg \beta_{111}^*$	$\lg \beta'$	$\lg \beta' \alpha_{As} \alpha_L$	$\lg \beta_{111}$
4.00	2.32	16.57	20.57	2.30	16.55	20.55
4.25	2.42	16.38	20.63	2.29	16.25	20.55
4.50	2.83	16.50	21.00	2.65	16.32	20.82
4.75	2.62	16.04	20.79	2.44	15.86	20.61
5.00	2.52	15.69	20.69	2.43	15.60	20.60
5.25	2.60	15.54	20.79	2.40	15.34	20.59
5.50	2.58	15.30	20.80	2.37	15.09	20.59
5.75	2.50	15.03	20.78	2.33	14.86	20.61
6.00	2.18	14.55	20.55	2.24	14.61	20.61
6.25	2.24	14.48	20.73	2.28	14.52	20.77
6.50	2.24	14.08	20.58	2.17	14.01	20.51

where the intercept is equal to $\lg \beta_{111}$ and the slope — to $j - i = 1$. The difference between both lines was found to be determined only by random errors¹⁷.

Hence, if $j = 2, i = 1$, the predominant protonated complex is $As(OH)_2 HL^{-2}$. The overall stability constant of this complex, β_{111} , was calculated from eqn. 2 using the data of β' obtained by both procedures and are given in Table 2. The mean values are $\lg \beta_{111}^* = 20.72 \pm 0.09$ for the first method, based on eqn. 3, and $\lg \beta_{111} = 20.62 \pm 0.06$ for the second method, based on the extrapolation functions. The statistical analysis of the data, obtained by both methods, showed that there is no difference between the mean values of the stability constants, since $F = 1.86 < F(95\%, f_1 = 10, f_2 = 10) = 2.97$ and $t = 2.00 < t(95\%, f = 20) = 2.09$.

As(III) — H_2T System

Figure 3 shows typical polarograms of As(III)- H_2T solutions. The half-wave potential is shifted to more negative values and the limiting diffusion current reaches a constant value \bar{i}_{As} when all arsenite is complexed (see also Fig. 4). The pH-range investigated was 4.0 — 5.5 at intervals of 0.25. Table 3 compares the results obtained under the same experimental conditions for the systems As(III)-DCTA and As(III)- H_2T . The data clearly show that the optimum condition for β' is satisfied only for the system As(III)-DCTA, whereas the precision of all β' -values, obtained for the As(III)- H_2T system remained poor since the complex was too weak. For the latter system, the statistical analysis¹⁷ of the results revealed a systematic error in β' -values, depending on the $\bar{i} - \bar{i}_0$ -values (see eqn 5). When the same experimental data were treated using the extrapolation method, the results for β' were more precise because the optimum conditions of this calculation method

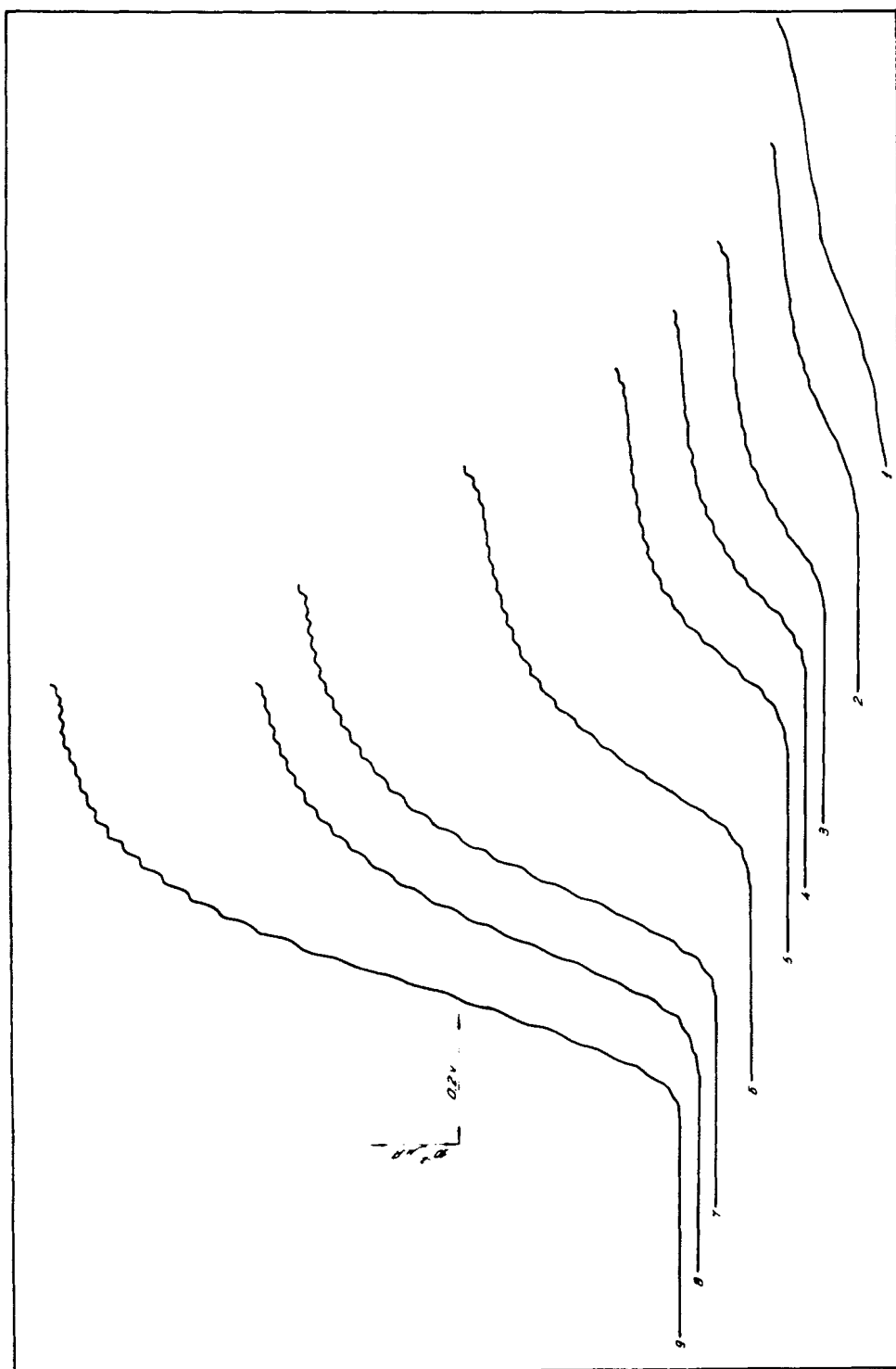


FIGURE 3 DC-Current-voltage curves of As(III)-H₂T complex at pH 4.75 in solutions containing 4.10⁻⁴ M As(III) and varying CH₂T, M × 10³: 1 - 0; 2 - 0.8; 3 - 1.6; 4 - 2.4; 5 - 3.2; 6 - 4.0; 7 - 6.4; 8 - 10.0; 9 - 16.0 recorded from -0.4 v (8cc).

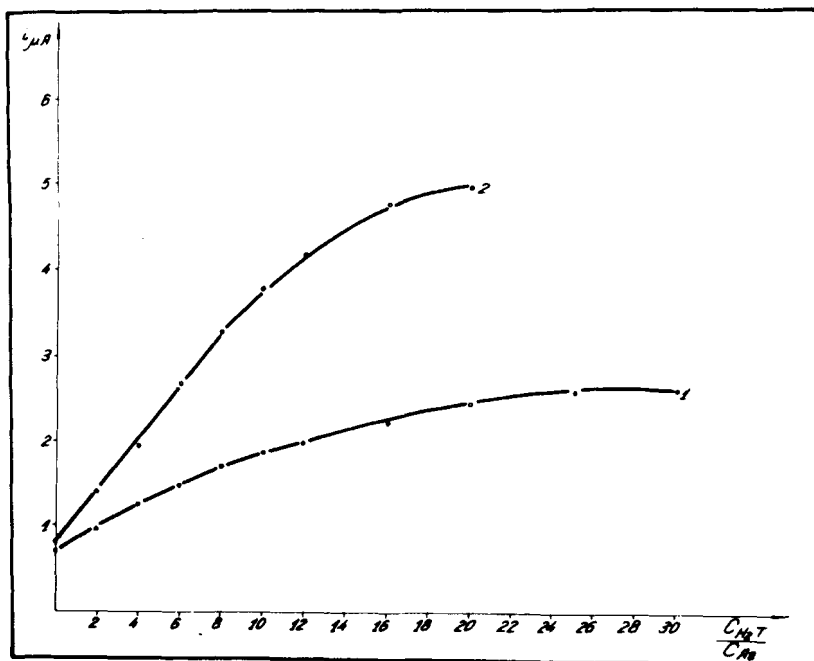


FIGURE 4 The limiting current plotted against the ratio C_{H_2T} / C_{As} at pH 4.00 in: 1 - $2.0 \cdot 10^{-4}$ M As(III) and 2 - 3.10^{-4} M As(III) - solutions.

TABLE III
Comparison of the limiting currents, measured for As(III)-DCTA and As(III)- H_2T systems at pH = 5.50

As(III)-DCTA $\bar{i}_{As} = 10.69 \mu A; C_{As} = 6.04 \cdot 10^{-4} M$ $\bar{i}_0 = 0$ $m = 1.20 \text{ mg/sec. } t = 4.70 \text{ sec.}$		As(III)- H_2T $\bar{i}_{As} = 5.05 \mu A; C_{As} = 3.00 \cdot 10^{-4} M$ $\bar{i}_0 = 0$ $m = 1.30 \text{ mg/sec; } t = 4.80 \text{ sec.}$	
C_{DCTA} $\times 10^3 M$	\bar{i} μA	C_{H_2T} $\times 10^3 M$	\bar{i} μA
9.0	8.550	12.0	0.675
7.5	7.125	9.0	0.375
6.0	6.225	7.5	0.345
4.5	5.475	6.0	0.173
3.0	4.050	4.8	0.225
2.4	3.150	3.6	0.120
1.5	2.025	3.0	0.165
0.6	0.825	2.4	0.135
		1.8	0.180

were fulfilled. From the extrapolated values of the f_1' functions at pH 4.0 and 4.25, the Ilkovich constant, \mathcal{H}_1 , was first calculated and found to be $1.67 \cdot 10^4$ (Table 4). The same table shows the β' -values calculated using eqn 10. According to the same equation with $\mathcal{H}_1 / \mathcal{H}_1 \cdot C_{As} \ll 1$ no iterative procedure is necessary, since $[L] = C_L$. In our case

this condition was satisfied for the experiments carried out at pH > 4.5. For this pH-range, the As(III)- H_2T complex was so weak that the product $\beta' \cdot C_L$ remained smaller than unity and the denominator of eqn 6 became equal to unity. In this manner the results of calculations for f_1 were practically unaffected by C_L and by C_{As} and equal to

TABLE IV
Data for the conditional stability constant, $\lg \beta'$, found from the extrapolated values of the functions f_1 and f_1' at various pH and As(III) concentrations

$C_{As} \times 10^{+4} M$	pH = 4.00			pH = 4.25			pH = 4.75			pH = 5.00			pH = 5.25			pH = 5.50		
	$\frac{\alpha_1}{\mathcal{N}_1} \times 10^{-6}$	$\mathcal{N}_1 \times 10^{-4}$	$\frac{\alpha_1}{\mathcal{N}_1} C_{As}$	$\lg \beta'$	$\frac{\alpha_1}{\mathcal{N}_1} \times 10^{-6}$	$\frac{\alpha_1}{\mathcal{N}_1} C_{As}$	$\lg \beta'$	$f_1 \times 10^{-5}$	$\lg \beta'$	$f_1 \times 10^{-5}$	$\lg \beta'$	$f_1 \times 10^{-5}$	$\lg \beta'$	$f_1 \times 10^{-5}$	$\lg \beta'$	$f_1 \times 10^{-5}$	$\lg \beta'$	$f_1 \times 10^{-5}$
5	2.6	1.08	0.12	2.44	0.5	1.00	1.70	3.4	1.30	2.4	1.15	1.0	0.78	1.0	0.7			
4	2.1	1.40	0.06	2.20	1.65	1.90	1.96	6.1	1.57	4.0	1.38	2.2	1.13	—	—			
3	4.2	1.84	0.07	2.25	1.10	1.85	1.84	5.8	1.54	5.7	1.53	2.5	1.17	1.6	1.0			
2	6.4	1.92	0.06	2.48	1.65	2.35	1.85	3.4	1.30	5.8	1.53	3.0	1.25	2.0	1.0			

TABLE V
Logarithmic values of overall stability constant, β_{101} , at various pH and As(III)-concentrations

pH	4.00	4.25	4.75	5.00	5.25	5.50
$C_{As}(M)$						
2.10^{-4}	6.92	6.46	6.36	6.84	6.80	6.58
3.10^{-4}	6.69	6.45	6.61	6.84	6.72	6.45
4.10^{-4}	6.64	6.57	6.63	6.69	6.68	6.80
5.10^{-4}	6.88	6.31	6.36	6.46	6.33	6.88

$\mathcal{N}_1 \beta'$ (Table 4). However, the conditional stability constant can be found if one takes \mathcal{N}_1' value, estimated at pH < 4.50. The $\alpha_{L(H)}$ values were calculated from the constants $K_1 = 9, 1.10^{-4}$ and $K_2 = 4, 3.10^{-5}$ ¹⁸. The mean values of $\lg \beta' \cdot \alpha_{As(OH)_2} \cdot \alpha_{L(H)}$ when plotted against pH gave a straight line with zero slope over the whole pH-range. This result suggests that the $As(OH)_2 T^{-1}$ -complex is the predominant species under the experimental conditions. The overall stability constant of this complex, β_{101} , was calculated from eqn 2 and the individual values are given in Table 5. To test the identity of all β_{101} -values an analysis of variance was made with the data distributed into six groups according to the six pH-levels. The Bartlett criterion showed that the data were homogeneous $\chi^2 = 1.73 < \chi^2 (P = 95\%, f = 5) = 11.1$. The variance S_1^2 within the groups was then compared with the variance S_2^2 between the groups by means of the Fischer test $F = 2.41 < F (P = 95\%, f_1 = 5, f_2 = 18) = 2.77$. The analysis of variance showed that the average value for the different pH-values did not differ more among themselves than would be expected, considering the precision of the method. The overall stability constant obtained as a mean value from all measurements was $\lg \beta_{101} = (6.62 \pm 0.14)$ at $\mu = 0.1$ and $t^\circ 25.0 \pm 0.2^\circ C$.

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