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NOTE

Electrochemical Study of In(III) Complexes with Oxytetracycline at Dropping Mercury Electrode

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In(III)-oxytetracycline system has been studied polarographically in aqueous medium at 32 and 40°C. The reduction of In(II) is quasi-reversible, diffusion-controlled involving three electron transfer process. Potential *vs.* current data at $\mu = 0.1$ M (KNO_3) have been interpreted on the basis of the stepwise formation of three complex species employing Deford and Hume's method. The logarithms of stability constant (log β) of binary complexes of In(III) at 32 and 40°C are 4.8451, 9.3979 and 14.1461 and 4.6021, 9.000 and 14.1303, respectively. The values of ΔG, ΔH and ΔS at 40°C are also reported.

Key Words: Stability constants, In(III)-oxytetracycline system, Thermodynamic parameters.

Antibiotics are used in several diseases in plants, animals and human beings[1, 2]. The *in vitro* activity has been found to be effective with lower concentration of antibiotics. The tetracyclines are strong chelating agents[3, 4] and both their antimicrobial and pharmacokinetic properties are influenced by chelation of metal ions. Tetracycline derivatives form chelation complexes with divalent cations[5–7]. Polarographic technique has already been used for the determination of stability constants (log β) of ternary complexes with different antibiotics[8, 9]. The stability of complexes of tetracycline and oxytetracycline with Cu(II), Pb(II) and UO_2(II) were studied by D.C. polarography and differential pulse polarography[10]. Stability constants (log β) of simple complexes of In(III) with N-glycylglycine, L-glutamine and L-asparagine have already been determined[11, 12]. In this paper, the binary complexes of In(III) with oxytetracycline at two different temperatures to determine the values of stability constants and thermodynamic parameters have been reported.

All chemicals used were of analytical reagent grade purity. Their solutions were prepared in double distilled water. The current-potential data for test solutions were recorded after passing pure nitrogen gas in the test solutions and 0.002% triton-x-100 was used as maximum suppressor. A digital D.C. polarograph (CL 357) was used to record the current voltage data. The capillary had the following characteristics: $m = 3.66$ mg/sec, $t = 3$ sec at 0.3 V *vs.* SCE. The depolarizer and ligand (antibiotic) were taken a definite ratio. The concentration of antibiotic was varied from 2×10^{-5} to 10×10^{-5} M. The pH of the test solutions was adjusted in the range of (2.10–3.75) ± 0.02 using dilute HCl/NaOH solutions.

Tables 1 and 2 summarize the polarographic results obtained for complexes of In(III) with oxytetracycline at 32 and 40°C in aqueous medium. The reduction of

In(III) at varying [ligand] was found to be quasi-reversible and diffusion controlled. The $(E_{1/2})_r$ values were determined by Gelling's method[13]. The $(E_{1/2})_r$ values were found to be shifted towards more negative potential with the increasing [ligand] due to complex formation. A plot of $(E_{1/2})_r$ as a function of log [ligand] showed the curvature expected for the formation of successive complexes. In order to derive the elaborate calculations of successive complex formation, Deford and Hume's method[14, 15] was adopted. Functions $F_j(x)$ are explained as

$$F_0(x) = \text{antilog}\,\{0.4343nF/RT[(E_{1/2})^0_S - (E_{1/2})^0_C] + \log I_S/I_C\} \quad (1)$$

$$F_0(x) = 1 + \beta_1[x] + \beta_2[x]^2 + \ldots + \beta_N[x]^N \quad (2)$$

$$F_1(x) = [(F_0x) - 1]/[x] \quad (3)$$

$$F_1(x) = \beta_1 + \beta_2[x] + \ldots + \beta_N[x]^{N-1} \quad (4)$$

$$F_2(x) = [(F_1x) - \beta_1]/[x] \quad (5)$$

$$F_2(x) = \beta_2 + \beta_3[x] + \ldots + \beta_N[x]^{N-2} \quad (6)$$

$(E_{1/2})^0_S$ and $(E_{1/2})^0_C$ are the half-wave potentials for the uncomplexed and complexed metal ions respectively. I_S and I_C are the diffusion current constants of these species and x is the concentration of ligand. The plot of $F_3(x)$ *vs.* [ligand] gave a horizontal line indicating the formation of only three complexes.

TABLE-1

In(III)-OXYTETRACYCLINE SYSTEM

$In^{3+} = 0.001$ M, $\mu = 0.1$ M KNO_3 at 32°C

[Oxy] $\times 10^{-3}$ M	$(\Delta E_{1/2})_r$ −V *vs.* SCE	log I_M/I_C	$F_0(x)$	$F_1(x)$ $\times 10^5$	$F_2(x)$ $\times 10^9$	$F_3(x)$ $\times 10^{12}$
0.00	—	—	—	—	—	—
0.02	0.012	0.0596	4.52	1.76	5.3	140.00
0.04	0.023	0.0859	16.91	3.98	8.2	142.50
0.06	0.032	0.0660	45.22	7.37	11.12	143.62
0.08	0.039	0.0532	97.77	12.10	14.25	146.88
0.10	0.044	0.0532	173.18	17.22	16.52	140.20

$\log \beta_1 = 4.8451$, $\log \beta_2 = 9.3979$ and $\log \beta_3 = 14.1461$

TABLE-2

In(III)-OXYTETRACYCLINE SYSTEM

$In^{3+} = 0.001$ M, $\mu = 0.1$ M KNO_3 at 40°C

[Oxy] $\times 10^{-3}$ M	$(\Delta E_{1/2})_r$ −V *vs.* SCE	log I_M/I_C	$F_0(x)$	$F_1(x)$ $\times 10^5$	$F_2(x)$ $\times 10^9$	$F_3(x)$ $\times 10^{12}$
0.00	—	—	—	—	—	—
0.02	0.010	0.0300	3.26	1.13	3.65	132.50
0.04	0.022	0.0404	12.74	2.94	6.35	133.75
0.06	0.031	0.0566	36.05	5.84	9.07	134.50
0.08	0.038	0.0678	80.70	9.96	11.95	136.88
0.10	0.044	0.0566	153.46	15.25	14.85	138.50

$\log \beta_1 = 4.6021$, $\log \beta_2 = 9.00$ and $\log \beta_3 = 14.1303$

The values of ΔG, ΔH and ΔS of complex formation were determined at 40°C (by standard equations) and are given in Table-3. A large negative value of standard entropy corresponds to a highly ordered activated complex and this implies a small value of steric factor.

TABLE-3
THERMODYNAMIC PARAMETERS FOR In(III)-OXYTETRACYCLINE SYSTEM

Composition of complex	Stability constants		ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/degree/mol)
	32°C	40°C			
1 : 1	4.8451	4.6021	–6.5871	–57.4509	–162.5042
1 : 2	9.3979	9.0000	–12.8820	–56.9821	–140.8949
1 : 3	14.1461	14.1303	–20.2251	–54.6305	–109.9214

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