POLAROGRAPHIC BEHAVIOUR OF THALLIUM(I) - δ - VALEROLACTAM SYSTEM

Ashok Kumar

Department of Chemistry, Devi Ahilya Vishwavidyalaya, Indore - 452 001.

In continuation of our earlier polarographic studies [1-4] with ε - caprolactam and pyrrolidinone-2, the polarographic behaviour of thallium(I) with δ-valerolactam has been studied in this work. The wave is irreversible, Kinetic parameters such as forward rate constant ($k^{\circ}_{f,h}$) and charge transfer coefficient (αn) have been calculated by using Koutecky's treatment as extended by Meites and Israel. Conditions have been developed for the determination of the metal individually and in synthetic samples. The interferences due to various ions have been studied in detail. Thermodynamic parameters such as $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$ have also been calculated at 303.15°K.

EXPERIMENTAL

Reagents

The stock solution of δ-valerolactam (Fluka, GR grade) was prepared in double distilled water. A solution of thallium was prepared by dissolving thallous nitrate (BDH, A.R) in distilled water and standardized [5]. PH of the solutions were adjusted with aqueous solutions of ammonia or perchloric acid. Ionic strength was maintained constant at 0.1 M with potassium nitrate.

Apparatus

A balancing type [6,7] manual polarograph was set up to obtain current - potential curves. The potential of the dropping electrode was measured against normal calomel electrode separated from the measured solution by a salt bridge filled with 1 M KCl

The polarographic cell was provided with a thermostat (accuracy ± 0.1° C). pH of the test solution was measured with an Elico pH meter. Oxygen was expelled by passing a slow stream of purified nitrogen through the test solution for 5 min. The capillary constants were m = 3.0 mg/S and t = 2.9 S at a height of mercury column 50 cm. The number of electrons (n) involved in the reduction process was determined by the millicoulometric method of De Vries and Kroon [8].

RESULTS AND DISCUSSION

The polarograms of the solution containing 1 mM of Tl(I) in 0.1 M KNO_3 and 0.1 M δ-valerolactam were taken at pH values between 4.5 and 6.0. The wave merges with the hydrogen wave below pH 4.5 and precipitation starts above pH 9.0. It was observed that the negative shift in $E_{1/2}$ was maximum at pH 6.5. Hence this pH value was chosen to study the polarography of thallium(I) - δ - valerolactam complexes. The diffusion current constant over the concentration range 0.5 to 4 mM of the metal ion in media of pH 6.5 was found to be 1.36.

Wave height for 1 mM metal - δ-valerolactam solution at pH 6.5 is directly proportional to the square root of the height of the mercury column in the range 35 - 80 cm. It indicates that the reduction of the metal ion is diffusion controlled.

The shape of the wave does not change when the δ-valerolactam concentration is varied from 0.1 to 0.5 M. The formation of the complex is evident as the half-wave potential is shifted to more negative side (Table 1) with increasing concentration of δ-valerolactam. The various reversibility criteria [9,10] indicates that the reduction process is irreversible. Kinetic parameters ($k^{\circ}_{f,h}$) and (αn) have been calculated by applying Koutecky's theoretical treatment as extended by Meites and Israel [11].

A perusal of the data in Table 1 shows a decrease in charge transfer coefficient (αn) and rate constant ($k^{\circ}_{f,h}$) with increasing concentration of δ-valerolactam, indicating the tendency of the wave towards irreversibility.

TABLE 1

POLAROGRAPHIC CHARACTERISTICS AND KINETIC PARAMETERS

Tl(I) = 1.0 mM, pH = 6.5, μ = 0.1 M KNO_3, n = 1

δ-valerolactam (M)	i_d (μA)	$-E_{1/2}$ vs SCE	Slope (mV)	$Do_3^{1/2} \times 10^3$ (cm^2/S)	αn	$k^{\circ}_{f,h} \times 10^6$ (cm/S)
0.1	3.25	0.512	105	1.89	0.516	3.57
0.2	3.20	0.528	108	1.87	0.502	3.00
0.3	3.20	0.532	109	1.87	0.497	2.93
0.4	3.18	0.545	111	1.85	0.488	2.50
0.5	3.16	0.560	113	1.84	0.480	2.07

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TABLE 2

DETERMINATION OF THALLIUM IN SYNTHETIC SAMPLE

δ -Valerolactam = 0.1 M, μ = 0.1 M KNO_3
Composition

Sample 1 Ni = 12.5, Co = 5.5, Mg = 16.4,
Zn = 1.6, Fe = 51.5, Tl = 3.5

Sample 2 Pt = 20.0 V = 9.5 , Pd = 15.5,
Ir = 28.0, W = 10.0, Tl = 17

	Amt. of Tl (mg) Taken	Found*	Error (%)
Sample 1	1.375	1.378 ± 0.005	+0.22
Sample 2	2.550	2.545 ± 0.006	-0.20

*Result of 10 replicate determinations

General Procedure for the Determination of Thallium(I)

The i_d values of polarograms were plotted against concentration of the metal ions, in media of pH 6.5 and then polarogram of the solution containing the metal in unknown concentration was recorded under identical conditions. The i_d values of this wave were referred to calibration curve and the concentration of the metal in the solution was determined. The results obtained are reproducible and accurate. The method has also been extended to the determination of thallium in synthetic sample.

Effect of Diverse Ions

The anions such as acetate, citrate, fluoride, formate, oxalate, nitrate, salicylate and sulphate do not affet the $E_{1/2}$ value. Ni,Co,Mn,Te, Zr,W,Cr,Fe,SC,Yb,V and As do not interfere upto five fold exceses. Only U(IV), Pb(II) and Cd(II) interfere in the determination but their lower amount of U (0.05 mg) and Cd (0.75 mg) could be tolerated. Alkaline earth metals Ba, Ca and Sr do not interfere in the determination, of the thallium upto 10 fold amounts.

Determination of Thermodynamic Parameters

The thermodynamic parameters, viz, the free energy of activation ($\Delta G^{\neq}$), the enthalpy of activation ($\Delta H^{\neq}$) and the entropy of activation ($\Delta S^{\neq}$) have been calculated by the methods reported in literature [12]. The reduction of thallium(I) at dme is diffusion - controlled at 293.15°K, 303.15°K, 313.15°K and 323.15°K as is shown by the linearity of i_d values versus $h^{1/2}$ plots. This is also supported by the fact that the temperature coefficient is found to be 1.36% over the temperature range 295 - 323°K. The value of $k^{\circ}_{f,h}$ for the electrode reaction of Tl(I) increases, as the temperature is raised, thereby, suggesting that electrode reaction tends to become less irreversible as the temperature is raised.

TABLE 3

KINETIC PARAMETERS AND THERMODYNAMIC FUNCTIONS AT VARIOUS TEMPERATURES

Tl(I) = 1.0 mM, μ = 0.1 M KNO_3, pH = 6.5, n = 1

Temp. (° K)	i_d (uA)	$-E_{1/2}$ vs SCE (V)	αn	$k^{\circ}_{f,h}$ (cm/S)
293.15	2.78	0.536	0.502	2.22×10^{-6}
303.15	3.25	0.512	0.516	3.53×10^{-6}
313.15	3.70	0.488	0.531	6.75×10^{-6}
314.15	4.18	0.465	0.542	9.45×10^{-6}

$\Delta H^{\neq}$ = 9.16 Kcal/mol $\Delta G^{\neq}$ = 10.34 Kcal.mol
$\Delta S^{\neq}$ = 38.94 cals/ deg/mol

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