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Electrokinetic Study of Gallium(III) with DL α-Alanine in Aqueous and 25% Ethanol in Water (v/v) at d.m.e.

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The polarographic behaviour of gallium(III) in DL α-alanine in aqueous and 25% ethanol-water (v/v) media has been studied. The reduction of Ga(III) (1 mM) has been found to be irreversible and diffusion controlled in the presence of 0.1 M KCl and 0.002% triton-X-100. The values of kinetic parameters, transfer coefficient (α_n) and formal rate constant ($k^0_{f,h}$) of the electrode reactions have been calculated by Koutecky's method. The values of thermodynamic parameters, the free energy of activation ($\Delta G^{\neq}$), the enthalpy of activation ($\Delta H^{\neq}$) and the entropy of activation ($\Delta S^{\neq}$) have also been determined at 30°C.

Key Words: Electrokinetic study, Gallium(III), DL-α-alanine.

INTRODUCTION

The study of metal-amino complexes is of great importance from biological point of view as it contributes to a better understanding of metal-protein interactions. A number of electrochemical studies on the behaviour of amino acids and their complexes[1–7] have been already carried out in this laboratory, which have been found useful for application in biochemistry and medicine[8]. From the survey of chemical literature[9–11] it has been found that comparatively few references are available in literature regarding polarographic studies of Ga(III) with DL α-alanine in aqueous as well as in the aqueous mixture of 25% ethanol[12–14]. The present study has therefore been undertaken to determine the polarographic characteristics and kinetic parameters of Ga(III) with varying ligand concentration in aqueous as well as non-aqueous mixture of 25% ethanol media.

EXPERIMENTAL

All the chemicals used were of analytical grade and the stock solutions were prepared in double distilled water. Ionic strength was maintained constant using KCl. The concentrations of metal ion, KCl, and triton-x-100 in test solutions were 1.0 mM, 0.1 M, 0.002% respectively.

An Elico digital polarograph (CL-357) was used for recording the current-voltage curves. Purified nitrogen was used for removing the dissolved oxygen. The potentials were measured against a saturated calomel electrode (S.C.E.). Triton-X-100 (0.002%) was used as the maximum suppressor. The pH of the test solutions was adjusted to 3.5 using dil. HCl/NaOH solutions. The capillary characteristics.

$$m = 4.66 \text{ mg/sec.}, \quad t = 3 \text{ sec.}, \quad m^{2/3}t^{1/6} = 3.350 \text{ at } h_{Hg} = 100 \text{ cm}$$

RESULTS AND DISCUSSION

Ga(III) in presence of DL α-alanine in aqueous as well as in the aqueous mixture of 25% ethanol produce a single well defined irreversible cathodic wave in 0.1 KCl as supporting and 0.002% triton-X-100 as maximum suppressor at pH-3.5.

The number of electrons (n) involved in the electro-reduction was determined by millicoulometric method[15] and was found to be 3 for Ga(III) knowing the value of n, the diffusion coefficient ($D^{1/2}$) of the depolariser was calculated by Ilkovic equation at different concentration of DL α-alanine. Log plot shows that the reduction is irreversible (slopes are in the range 108–117 mV). The current at the end of the drop life was recorded instead of the average current, because the determination of kinetic parameters is based on the Koutecky's method[16] which is more accurately reproduced by measuring the maximum current[17].

The plots of i_d *vs.* $h_{eff}^{1/2}$ were found to be linear and passing through the origin, thereby indicating the diffusion controlled nature of the reduction. The various criteria[18–21] of irreversibility indicate that the electrode reactions of Ga(III) are irreversible.

From Tables 1 and 2 it is clear that the value, of $-E_{1/2}$ are higher in 25% ethanol in water (v/v) than those in the aqueous media at the same ligand concentration whereas i_d decrease. This is due to the increase in viscosity at 25% ethanol in water (v/v) than those in aqueous media. $E_{1/2}$ is affected by ion-pair formation in low dielectric constant which is 24.3 for ethanol as compared to 81 for water, *i.e.*, stability of the complex species is enhanced with the lowering of the dielectric constant of the medium[22]. The values of α_n and $K^0_{f,h}$ calculated in aqueous and 25% ethanol-water (v/v) media at 30°C are presented in the Tables 1 and 2.

TABLE-1
POLAROGRAPHIC CHARACTERISTICS AND KINETIC PARAMETERS FOR Ga(III)-DL α-ALANINE SYSTEM AT 30°C IN AQUEOUS MEDIA

Conc. of DL α-alanine (M)	i_d (μA)	$D^{1/2}$ ($cm/sec^{1/2}$)	Intercept $-E_{1/2}$ (V)	α_n	$\log K^0_{f,h}$	$K^0_{f,h}$ (cm/sec)
0.0010	7.35	1.200	1.135	0.497	–7.79	1.58×10^{-8}
0.0015	7.15	0.781	1.138	0.488	–7.87	1.33×10^{-8}
0.0020	6.45	0.528	1.142	0.483	–7.97	1.07×10^{-8}
0.0025	6.35	0.416	1.146	0.471	–8.08	8.29×10^{-8}
0.0030	5.10	0.278	1.155	0.473	–8.23	5.83×10^{-9}
0.0040	4.35	0.178	1.160	0.463	–8.33	4.87×10^{-9}

TABLE-2
POLAROGRAPHIC CHARACTERISTICS AND KINETIC PARAMETERS FOR Ga(III)-DL α-ALANINE SYSTEM AT 30°C IN 25% ETHANOL MEDIA

Conc. of DL α-alanine (M)	i_d (μA)	$D^{1/2}$ (cm/sec$^{1/2}$)	Intercept $-E_{1/2}$ (V)	α_n	$\log K^0_{f,h}$	$K^0_{f,h}$ (cm/sec)
0.0010	7.15	1.172	1.140	0.483	–7.64	2.27×10^{-8}
0.0015	7.00	0.764	1.142	0.475	–7.71	1.90×10^{-8}
0.0020	6.40	0.524	1.145	0.471	–7.85	1.41×10^{-8}
0.0025	6.25	0.409	1.148	0.471	–7.98	1.04×10^{-8}
0.0030	5.00	0.273	1.158	0.463	–8.11	7.75×10^{-9}
0.0040	4.30	0.176	1.162	0.459	–8.41	3.85×10^{-9}

$E_{1/2}$ values shifted to more negative potentials with increasing ligand concentration revealing complex formation. A perusal of the values of α_n reveals that α_n decreases with increasing concentration of DL α-alanine, which implies[23] that the transfer of electron is made inceasingly difficult. In other words, the electrode reaction of Ga(III) is rendered increasingly irreversible with increase in ligand concentration. Decreasing value of $k^0_{f,h}$ also indicates[24] the increased irreversibility of the electrode reaction of Ga(III) with increasing concentration of DL α-alanine.

Table-3 shows the effect of temperature on different parameters. The perusal of Table-3 shows that $E_{1/2}$ value shifts to more positive value as the temperature is raised. This indicates the easier reduction of Ga(III) DL α-alanine system at the d.m.e. and this observation is in agreement with the view of Brdicka[25]. The values of α_n and $k^0_{f,h}$ show an increase with the temperature, thereby suggesting that electrode reaction of Ga(III) DL α-alanine system tends to become less irreversible as the temperature is increased.

TABLE-3
POLAROGRAPHIC CHARACTERISTICS AND KINETIC PARAMETERS OF THE ELECTRODE REACTION OF Ga(III) IN DL α-aLANINE (0.003) AT DIFFERENT TEMPERATURES

Polarographic characteristics	Ga(III) in aqueous media		Ga(III) in 25% ethanol media	
	30°C	40°C	30°C	40°C
$E_{1/2}$(V)	1.155	1.140	1.158	1.142
Id (μA)	5.100	5.300	5.000	5.200
α_n	0.473	0.479	0.463	0.471
$D^{1/2}$ (cm/sec$^{1/2}$)	0.278	0.289	0.273	0.284
$\log k^0_{f,h}$	–8.230	–8.190	–8.110	–8.090
$k^0_{f,h}$ (cm/sec)	5.83×10^{-9}	6.43×10^{-9}	7.75×10^{-9}	8.08×10^{-9}

Since Ge(III) reduces irreversibly at d.m.e. in DL α-alanine media, Koutecky treatment[16] as extended by Meites and Israel[17] is applied for determining the kinetic parameters, *viz.*, transfer coefficient (α_n) and formal rate constant ($k^0_{f,h}$) for electrode reaction by using the equation:

$$E_{d.e.} = E_{1/2} - \frac{0.0542}{\alpha_n} \log \frac{i_d}{(i_d - i)}$$

where

$$E_{1/2} = -0.2412 + \frac{0.05915}{\alpha_n} \log \frac{1.349\, k^0_{f,h} t^{1/2}}{D^{1/2}}$$

The value of α_n was determined by equating the slope of plots $-E_{1/2}$ *vs.* log i/I_{d-I} to $0.0542/\alpha_n$ and the intercept ($E_{1/2}$) was used to calculate $k^0_{f,h}$ at different concentration of ligand, after getting the values of $D^{1/2}$ from Ilkovic equation.

Thermodynamic Function

The enthalpy of activation ($\Delta H^{\neq}$) for the electrode reaction has been calculated by equating the slope of plot log $k^0_{f,h}$ vs 1/T to $-\Delta H^{\neq}/2.303$ R.

The free energy of activation ($\Delta G^{\neq}$) could be determined from the equation

$$K^0_{f,h} = \frac{kT}{h} \phi \exp\left[\frac{-\Delta G^{\neq}}{RT}\right]$$

where k = Boltzmann's constant, h = Planck's constant and $\phi = 2.0 \times 10^{-8}$ cm. The entropy of activation of ($\Delta S^{\neq}$) at 30°C calculated from the relation

$$\Delta S^{\neq} = \frac{\Delta H^{\neq} - \Delta G^{\neq}}{T}$$

A negative value of $\Delta S^{\neq}$ tends support to the irreversible electrode process in the present investigation.

Thermodynamic Function at Different Temperatures

Ga(III) = 1.0 mM, μ = 0.1 M KCl, pH = 3.5, n = 3

Parameters	DL α-Alanine in aqueous media	DL α-Alanine in 25% ethanol media
$\Delta H^{\neq}$ (kcal/mol)	1.83	1.52
$\Delta G^{\neq}$ (kcal/mol)	12.02	11.95
$\Delta S^{\neq}$ (cal/degree/mol)	–33.63	–34.42

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