Electrochemical studies of In (III) in presence of alizarin in aqueous-DMF (70:30) solvents mixture

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(Received: August 08, 2009; Accepted: October 15, 2009)

ABSTRACT

Indium (III) complex with Alizarin [1,2-Dihydroxyanthraquinone] have been investigated polarographically using Potassium Nitrate as supporting electrolyte in aqueous non-aqueous medium at 293 K and 303 K and pH 6.0 to 6.4. Indium (III) formed 1:1, 1:2 and 1:3 complex species in solution with Alizarin. DeFord and Hume’s method and Mihailove’s method have been applied for the determination of stability constants and kinetic parameters were evaluated for the reduction process at d.m.e. The stability constant of In (III) complexes with Alizarin at 303 K are 1.5502, 1.9701 and 4.4800 and by using Mihailov’s method are 1.4823, 2.9744 and 4.2904.

Key words: Electrochemical studies, Alizarin, DMF solvent mixtures.

INTRODUCTION

There have been a number of electroreduction studies on simple [1-4] and mixed [5-14] ligand complex formation by different methods. The polarographic behaviour of In (III) has been studied at D.M.E. and it was observed that In (III) reduced quasireversibly because at D.M.E. and it was observed that In (III) reduced quasireversibly because the plots of log i/id –i Vs E _d_e. were found to be linear. The reduction was found to be diffusion controlled as revealed from the straight line plot of id Vs square root of effective height of mercury column (H½ eff), in this paper the composition, stability constants and the kinetic parameters of Indium (III) with Alizarin have been reported.

EXPERIMENTAL

A. R. grade chemicals were used. The solvents used were purified by standard methods. The solutions contain 0.5 mM of In (III) and varying concentrations of Alizarin from 0.001 M to 0.009M. potassium nitrate of concentration 0.1 M was used as supporting electrolyte to maintain the constant ionic strength (µ=1) of the solution and 0.002% Triton X -100 was used as a maxima suppressor. A manual polarographic set up was used for recording polarograms. The dropping mercury electrode had the characteristics m = 1.75 mg/sec and t = 3.8 se. (in open circuit). The measurements were done at constant temperatures [293 K and 303 K] maintained by using Haake-type ultra-thermostat. Before examining the solutions polarographically, purified nitrogen gas was passed through each solution for 20-30 minutes (according to solvent) to remove dissolved oxygen. The gradual increase in current with increase in potential was recorded and plotted to obtain the polarogram for the solution. At this particular pH solutions were showing measurable negative shift in half-wave potential and decreasing diffusion current of In (III) on addition of the ligand Alizarin to solutions containing 0.5 mM In (III) in aqueous – DMF (30%) mixed solvent, confirmed complexations between In (III) and Alizarin in the mixed solvents mixture.

In (III) reduced quasireversibly and hence for each solution E_r½ values were obtained by Gellings method. DeFord and Hume’s method and Mihailov’s method were applied to determine the data regarding metal ligand ratios and overall stability constant of metal complexes.
The various polarographic measurements and $F_j(X)$ functions values at 293 K and 303 K have been recorded in Tables 1 and 2, respectively. The Mihailov's constants 'a' and 'A' at 293 K and 303 K have been recorded in Tables 1.1 and 2.1, respectively. The results have also been shown graphically in Figs. 1.2 and 2.2.

RESULTS AND DISCUSSION

The plots of $F_0(X)$ Vs $C_x$ were smooth curves in all solutions, showing the formation of more than one complexes in aqueous – DMF (30%) solvents mixture. Further analysis showed the presence of three consecutive complexes in mixed solvents medium, since the plots of $F_1(X)$ and $F_2(X)$ Vs ligand concentration (Alizarin) were a curve and a straight line with a slope, respectively and the plot of $F_3(X)$ Vs [Alizarin] was a straight line parallels to ligand concentration (axis) (without slope). The Plots of $F_j(X)$ Vs Alizarin on extrapolation to $[X] = 0$ resulted in the values of $\beta_j$.

The overall formation constants determined at 293K and 303 K enabled to calculate the thermodynamic functions values which are recorded below:

| Complex Species | $\Delta G^0$ (-) (K Cals/mol) | $\Delta H^0$ (-) (K Cals/mol) | $\Delta S^0$ (-) (Cals/mol/deg) |
|-----------------|-------------------------------|-------------------------------|---------------------------------|
| MX$_1$          | 2.0518                        | 39.3657                       | 0.1273                          |
| MX$_2$          | 3.8477                        | 40.2203                       | 0.1241                          |
| MX$_3$          | 5.7711                        | 40.4483                       | 0.1183                          |

M = Indium (III), X = Alizarin

The effect of non-aqueous solvents on the stability of the complexes depends on several factors such as dielectric constant, viscosity of the media, depolariser, ion-pair formation, the coordinating abilities of the non-aqueous solvent molecules and those of supporting electrolyte etc.

The cathodic shift in the half-wave potential indicates greater degree of complexation as the percentage of non-aqueous solvent is increased. This may be attributed to the decreasing dielectric constant of the medium, which results in less solvation of the metal ion In (III). This makes the
| $C_x$ (Moles/Litre) | $i_s$ (Divisions) | $E'_s$ (-v vs S. C. E.) | $F_s[(X)]$ | $F_1[(X)]$ | $F_2(X) \times 10^3$ | $F_3[(X)] \times 10^4$ |
|---------------------|-------------------|--------------------------|------------|------------|---------------------|---------------------|
| 0.000               | 58                | 0.5750                   | -          | -          | -                   | -                   |
| 0.001               | 56                | 0.5750                   | 1.0408     | 40.83      | 1.031               | 3.164               |
| 0.002               | 54                | 0.5751                   | 1.0838     | 40.83      | 1.063               | 3.168               |
| 0.003               | 53                | 0.553                    | 1.1292     | 41.92      | 1.095               | 3.172               |
| 0.004               | 52                | 0.5756                   | 1.1772     | 43.08      | 1.127               | 3.182               |
| 0.005               | 51                | 0.5756                   | 1.2279     | 45.59      | 1.159               | 3.186               |
| 0.006               | 49                | 0.5759                   | 1.2817     | 46.95      | 1.191               | 3.198               |
| 0.007               | 47                | 0.5760                   | 1.3385     | 48.36      | 1.223               | 3.199               |
| 0.008               | 46                | 0.5763                   | 1.3987     | 49.84      | 1.256               | 3.200               |
| 0.009               | 45                | 0.5765                   | 1.4626     | 51.40      | 1.289               | 3.213               |

$\log \beta_1 = 1.5498$  $\log \beta_2 = 3$  $\log \beta_3 = 4.4996$;  $C_x =$ Alizarin concentration, moles.litre$^{-1}$

| S. No. | Combinations of Alizarin Concentrations (Moles/Lit.) | ‘a’ | Concentration of Alizarin (Moles/Lit.) | ‘A’ |
|--------|-----------------------------------------------------|-----|---------------------------------------|-----|
| 1      | 0.001                                               | 47.69 | 0.001                                 | 0.7496 |
|        | 0.002                                               | 47.69 | 0.002                                 | 0.7475 |
|        | 0.003                                               | 47.69 | 0.003                                 | 0.7448 |
| 2      | 0.003                                               | 55.99 | 0.003                                 | 0.7448 |
|        | 0.004                                               | 55.99 | 0.004                                 | 0.7448 |
| 3      | 0.004                                               | 55.99 | 0.004                                 | 0.7448 |
|        | 0.005                                               | 55.99 | 0.005                                 | 0.7448 |
| 4      | 0.005                                               | 55.99 | 0.005                                 | 0.7448 |
|        | 0.006                                               | 55.99 | 0.006                                 | 0.7448 |
| 5      | 0.006                                               | 55.99 | 0.006                                 | 0.7448 |
|        | 0.007                                               | 55.99 | 0.007                                 | 0.7448 |
| 6      | 0.007                                               | 55.99 | 0.007                                 | 0.7448 |

Average ‘a’ = 53.25  Average ‘A’ = 0.7479

$\log \beta_1 = 1.5502$  $\log \beta_2 = 1.9701$  $\log \beta_3 = 4.4800$;  $C_x =$ Alizarin concentration, moles.litre$^{-1}$

| $C_x$ (Moles/Litre) | $i_s$ (Divisions) | $E'_s$ (-v vs S. C. E.) | $F_s[(X)]$ | $F_1[(X)]$ | $F_2(X) \times 10^3$ | $F_3[(X)] \times 10^4$ |
|---------------------|-------------------|--------------------------|------------|------------|---------------------|---------------------|
| 0.000               | 60                | 0.5730                   | -          | -          | -                   | -                   |
| 0.001               | 58                | 0.5730                   | 1.036      | 36.46      | 9.63                | 3.025               |
| 0.002               | 56                | 0.5730                   | 1.074      | 37.49      | 9.93                | 3.023               |
| 0.003               | 55                | 0.5732                   | 1.115      | 38.57      | 10.24               | 3.038               |
| 0.004               | 53                | 0.5733                   | 1.158      | 39.72      | 10.55               | 3.043               |
| 0.005               | 51                | 0.5733                   | 1.204      | 40.93      | 10.85               | 3.042               |
| 0.006               | 49                | 0.5733                   | 1.253      | 42.20      | 11.16               | 3.056               |
| 0.007               | 47                | 0.5732                   | 1.304      | 43.53      | 11.47               | 3.062               |
| 0.008               | 45                | 0.5732                   | 1.359      | 44.93      | 11.78               | 3.064               |
| 0.009               | 44                | 0.5735                   | 1.447      | 46.40      | 12.10               | 3.083               |
approach of the ligand towards metal ion easier and hence the complex is more stable.

The stability constants are higher in mixtures than purely aqueous medium. The greater stability of the complexes in DMF-Aqueous medium than in water may again be attributed to the less degree of solvation of In (III) which is due to lower values of dielectric constant than water (H' 80) and hence the complex is much stable in these solvents than in purely aqueous medium.

ACKNOWLEDGEMENTS

The authors are thankful to the Head, Chemistry Department, University of Rajasthan, Jaipur for providing the necessary facilities to carry out the research work.

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