TECHNICAL REPORT

FORMATION CONSTANTS & THERMODYNAMIC FUNCTIONS OF LEAD & CADMIUM IONS WITH QUINOLINATE IONS

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Cadmium and lead complexes with Quinolinate ions have been investigated polarographically in sodium perchlroate (μ 1.5) at 30° and 40°C. Cadmium forms four complex species, i.e. 1:2, 1:2, 1:3 and 1:4, which are in equilibrium, whereas lead forms five species. The overall formation costants in both the cases at 30° and 40°C have been evaluated by Deford and Hume treatment as modified by Irving. Thermodynamic functions ($\triangle H^\circ$, $\triangle F^\circ$ and $\triangle S^\circ$) have been calculated for both systems. The percentage composition of the various complexed and uncomplexed species in both the systems have also been calculated.

All the six isomeric dicarboxylic acids, except 3,5 – Pyridine dicarboxylic acid, are potentially capable of acting as bidentate chelating agents. Banerjee and and Ray[1] have determined the composition and stability of Fe (II) complexes with dipicolinic and quinolinic acid. Majumdar and Bag[2] have studied Fe (II) complexes of α-picolinic acid and quinolinic acid in the presence of cyanide ions. The step-wise formation constants of ferrous quinolinic acid complexes have been reported[3]. The stability constants of quinoline and lutidinic acid complexes with some bivalent metal ions have been determined by pH titration method[4]. The thermal properties of quinolinic and lutidinic acid complexes of divalent metal ions have been studied[5]. Recently the potentiometric and conductometric study of quinolinic acid complexes with Al (III), In (III) and La (III) has also been carried out[7]. From the foregoing review of literature it is evident that quinolinic acid complexes offer a wide field for further investigations. The present investigations are devoted to the polarographic behaviour of Cd (II) and Pb (II) ions with quinolinic acid.

Experimental

All the chemicals used were of reagent grade. Stock solutions of Cd (II) and Pb (II), M/40 each, were prepared from their respective nitrates. Sodium salt of quinolinic acid was used as complexing agent. Solutions containing lmM of metal ion with varying concentrations of quinolinate ions were prepared at constant ionic strength ($\mu = 1.5$) which was maintained by the addition of $NaClO_4$ solution. The pH of the solutions was kept at 6. 7 $\pm$ 0.1 with the addition of $HClO_4$ or NaOH solutions.

A manual polarographic set up was used for obtaining C–V curves. The dropping mercury electrode having the characteristics m = 1.76 mgm/sec, and t = 3.64 sec. (Open circuit) was used. All the measurements were performed at constant temperatures (30° and 40°C). Triton X—100 was used as maxima suppressor whenever needed. The polarograms were recorded after deaeration (20—25 minutes) of solutions with purified nitrogen. H-type cell with Agar-Agar plug saturated with NaCl served as electrolytic cell.

Results and Disscussions

In each case, a well defined diffusion controlled reduction wave appeared. The half-wave potential shifted towards more negative value and i_d was found to decrease with concentration of quinolinate ions, indicating complex formation. Plots of i_d vs h and i_d vs metal ion concentration were found to be straight lines passing through the origin, showing that the reductions are controlled by diffusion.

The plots of $E_{\frac{1}{2}}$ vs—log C_x (C_x is the quinolinate ion concentration in moles) were found to be smooth curves in all the cases, indicating the formation of two or more complex species which were in equilibrium. The method of Lingane[8] could not be applied for the determination of formation constants. For this purpose Deford and Hume treatment[9] for the stepwise formation constant has been applied. The details of of the method were published in an earlier paper[10].

The thermodynamic stability constants are related to other thermodynamic functions in the following manner :

$$\triangle F^\circ = -2.303\ RT \log (\beta_j)T$$

$$\triangle H^\circ = -2.303\ RT_1T_2\ (\log \beta T_1 - \log \beta T_2)/(T_2 - T_1)$$

$$\triangle F^\circ = \triangle H^\circ - T\ \triangle S^\circ$$

$\triangle F^\circ$ is the standard free energy change, $\triangle H^\circ$ is the change in heat content and $\triangle S^\circ$ is the change in entropy. β_j is the formation constants of j th order, βT_1 and βT_2 are the formation constants at temperatures T_1 and T_2 respectively.

Cd (II) — Quinolinate system

The plots of log $i/(i_{d-i})$ Vs $E_{d.e.}$ were linear with a slope 31 $\pm$ 2mV, indicating reversibility of the electrode

process involving two electrons. The results indicate the formation of four complex species: [Cd quinolinate], [Cd (quinolinate)$_2$]$^{-2}$, [Cd (quinolinate)$_3$]$^{-4}$ and [Cd (quinolinate)$_4$]$^{-6}$ having β_1, β_2, β_3 and β_4 as 5×10^3, 20×10^4, 120×10^4 and 640×10^4 at 30°C respectively. Again four species with $\beta_1 = 2\times10^3$, $\beta_2 = 18\times10^4$ $\beta_3 = 60\times10^4$ and $\beta_4 = 625\times10^4$ were formed at 40°C.

The above data shows that by increasing the temperature, the stability of the complexes decreases as expected. The distribution of metal ions present in the form of various species in the solution with logarithm of quinolinate ion concentration at 30°C have been determined. The values of thermodynamic functions ($\Delta H°$, $\Delta F°$ and $\Delta S°$) have been presented in Table I.

TABLE I Formation constants and Thermodynamic functions

Complex and its composition.	Formation Constants 30°C	40°C	$\Delta F°$ (K cal/mole)	$\Delta H°$ (K cal/mole)	$\Delta S°$ (cal/deg mole)
Cd (II)—quinolinate (1:4)	640×10^4	625×10^4	−9.73	−9.44	−29.60
Pd (II)—quinolinate (1:5)	215×10^3	77.5×10^3	−8.48	−1.48	−22.27

(Pb) II — Quinolinate System

Similar results were obtained with Pb (II) quinolinate system, where-in five complexes are found, which are in equilibrium. Values of β_1, β_2, β_3, β_4 and β_5 are equal to 7.5×10^2, 29×10^3, 80×10^3, 168×10^3 and 215×10^3 at 30°C and 38×10^2, 24×10^3, 36×10^3, 40×10^3 and 77.5×10^3 respectively at 40°C. The polarographic characteristics and F_o ([×]) values at 30° and 40°C are recorded.

Distribution of Pb (II) in various forms as a functions of logarithm of quinolinate ion concentration at 30° C have been determined. The values of thermodynamic functions were also calculated and incorporated in Table I.

Since all reductions were found to be diffusion-controlled both Cd (II) and Pb (II) can be estimated polarographically in the presence of quinolinate ions.

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