

POLAROGRAPHIC BEHAVIOUR OF METAL IONS IN SOME NITROGENOUS COMPOUNDS

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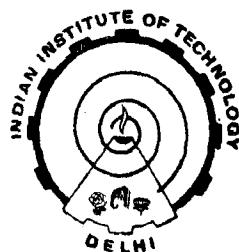
ASHOK KUMAR

DEPARTMENT OF CHEMISTRY

Submitted

in fulfilment for the requirements
of the degree of

DOCTOR OF PHILOSOPHY

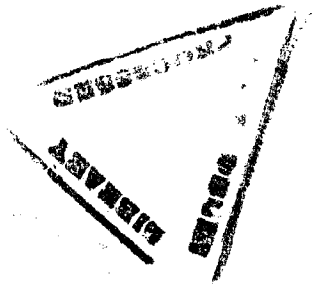


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Dedicated


to

My Parents

C E R T I F I C A T E

This is to certify that the thesis entitled, "Polarographic Behaviour of Metal Ions in Some Nitrogenous Compounds", being submitted by Mr. Ashok Kumar to the Indian Institute of Technology, Delhi for the award of the degree of 'Doctor of Philosophy', is a record of bonafide research work carried out by him. Mr. Ashok Kumar has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted in part or in full, to any other University or Institute for the award of any degree or diploma.



(Dr. B.K. Puri)
Thesis Supervisor

A C K N O W L E D G E M E N T S

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ABSTRACT

The thesis consists of six chapters; and each is subdivided into various sections.

A brief introduction to the fundamentals of polarography and scope of the present work is described in the first chapter.

The second chapter deals with the polarographic determination of zinc (II), cadmium (II), indium (III), gallium (III), lead (II), arsenic (III), vanadium (V), niobium (V), tellurium (IV), manganese (II), cobalt (II), nickel (II), palladium (II), europium (III) and uranium (VI) using ϵ -caprolactam as the complexing agent. Various parameters such as effect of pH, effect of ϵ -caprolactam concentration and metal ion concentration etc. have been studied. Interference of various ions have been studied in detail. These conditions have been utilized for the determination of some of these metals in various complex materials i.e. alloys.

Polarographic determination of the metals i.e. copper (II), thallium (I), antimony (III), lead (II), cadmium (II), cobalt (II), zinc (II), manganese (II), nickel (II), uranium (VI), palladium (II), tellurium (IV), europium (III) and gallium (III) using pyrrolidinone-2 as supporting electrolyte has been summarized in the third chapter. Various parameters similar to the

above have been evaluated and the conditions have been developed for the determination of these metals in certain complex materials.

Electro-chemical behaviour of lead(II), cadmium(II), zinc(II) and nickel(II) at d.m.e. using ϵ -caprolactam and pyrrolidinone-2 as the complexing agents has been discussed in fourth chapter. The stability constants have been evaluated by using Deford-Hume and Ringbom-Eriksson methods for reversible and irreversible systems respectively. The percentage distribution of various complex species present at different ligand concentrations have also been studied.

The fifth chapter starts with the brief introduction regarding the calculation of kinetic parameters i.e. forward rate constant ($k_{f,h}^0$) and charge transfer coefficient (α_n). These parameters have been calculated using Koutecky's theoretical treatment as extended by Meites and Israel for the metals, i.e. cobalt(II), zinc(II), nickel(II), manganese(II), palladium(II), uranium(VI), tellurium(IV), gallium(III) and indium(III) using ϵ -caprolactam and pyrrolidinone-2 as complexing agents.

The influence of temperature on the kinetics of irreversible electrode reactions of some metal ions

such as cobalt(II), zinc(II), manganese(II), uranium(VI), palladium(II), tellurium(IV) with ϵ -caprolactam and zinc(II), nickel(II), cobalt(II), manganese(II), uranium(VI), thallium(I), tellurium(IV) and palladium(II) with pyrrolidinone-2 has been studied polarographically and is being reported in the last chapter. Thermodynamic parameters i.e. free energy of activation (ΔG^\ddagger), enthalpy of activation (ΔH^\ddagger) and entropy of activation (ΔS^\ddagger) have been calculated.

Abbreviations and Symbols used

μA	microamperes
V	volts
i	current in μA passing through the system
E	potential in volts
t	drop time in seconds
m	rate of flow of mercury in mg/sec
i_d	diffusion-current
$E_{1/2}$	half-wave potential
n	number of electrons involved in the reaction process
α	transfer coefficient
N.H.E.	normal hydrogen electrode
S.C.E.	saturated calomel electrode
$k_{f,h}^0$	rate constant at 0 (zero) V vs. N.H.E. (-0.2412 V vs. S.C.E.)
C	concentration in millimoles/litre
D	diffusion coefficient in cm^2/sec
$E_{3/4}$	potential at $i = \frac{3}{4} i_d$
$E_{1/4}$	potential at $i = \frac{1}{4} i_d$
T	temperature in degree absolute
R	gas constant
F	Faraday
h_{corr}	corrected height of mercury column
C-V	current-voltage

d.m.e. dropping mercury electrode
 ΔG^\ddagger the free energy of activation
 ΔH^\ddagger the enthalpy of activation
 ΔS^\ddagger the entropy of activation
Cpl caprolactam

C O N T E N T S

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