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KINETICS OF ELECTROCRYSTALLISATION OF CALOMEL  
IN CHLORIDE SOLUTIONS UNDER POTENTIOSTATIC  
CONDITIONS

A thesis presented for the Degree of

MASTER OF SCIENCE

in the University of Ceylon, Colombo

by

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## ABSTRACT

A summary of the kinetics of chemical and electro-chemical reactions are discussed. In the next Chapter, the concepts of electrocrystallisation and factors that govern nucleation and growth are summarised. An introduction to the types of anodic electrocrystallisation reactions are then given. The theories that have been developed for the study of electrochemical reactions are discussed.

In the fourth Chapter, the techniques available for studying the kinetics of fast reactions are shown in detail. The basic equation for the current due to electrochemical reactions are given. The work done by various schools of research in this field, is summarised in the fifth Chapter. The present state of knowledge of the electrocrystallisation of calomel is discussed here.

The experimental technique used in the measurement of the  $i/t$  transient is detailed in the next Chapter. Results are obtained using a modified electrode for  $i/t$  transients for five different concentrations of HCl and  $\text{HClO}_4$ , namely 0.4M HCl, 1.0M HCl, 0.1M HCl + 0.9M  $\text{HClO}_4$ , and 1.0M  $\text{HClO}_4$ .

The next Chapter on Discussion and Interpretation of results shows our method of analysis of the  $i/t$  transients. The true electrocrystallisation transient is estimated from the observed transient. Different models were examined and a best fitting model is derived for the  $i/t$  variation in this transient. The importance of specific adsorption of chloride ions in electrocrystallisation is shown from a calculation of charge-transfer resistance. Our present studies on the anodic electrocrystallisation of calomel on mercury show that the Devanathan Ramasami model is correct.