

ACKNOWLEDGEMENTS

It is my duty to thank Professor J. S. Singh for permission to use the Physical Chemistry Laboratory facilities. His encouragement of, initiative and keen interest in my work are much appreciated.

THE SPECIFIC ADSORPTION OF TETRA ALKYL AMMONIUM IONS

AT THE MERCURY WATER INTERFACE

Sincere thanks are due to Dr. J. S. Singh for guidance and advice rendered during the course of the work. The author wishes to place on record his deep debt of gratitude for the personal interest which the supervisor has taken in this work and ready co-operation extended to him. It has indeed been a privilege and a great pleasure to do research under him.

A Thesis presented for the Degree of

Thanks are also due to Master of Science for assistance during the early stages of the activity coefficient determinations, Mr. Wijeweera for graphics in the University, Mr. H. S. Ceylon for technical assistance and Messrs C. Pushparatnam, H. A. Fernando, and V. Edwin for general assistance given.

by

M. JONAS FERNANDO, B.Sc. (Ceylon).

159687



ABSTRACT OF THE THESIS

CONTENTS

A historical survey of the structure of the electrical double layer is presented. A recent theory which satisfactorily explains the differential capacity taking into account the specific adsorption of the ions is discussed in detail. The thermodynamics of ideally polarizable interfaces is reviewed.

The Gibb's adsorption equation is made use of to derive an electro-capillary equation for the adsorption of tetra alkyl ammonium iodide at the Mercury water interface.

The details of the experimental technique used in determining electro-capillary curves are described. An e.m.f. method for determining activity coefficients of tetra alkyl ammonium salts is explained in detail.

Electro-capillary data for 21 solutions of the tetra alkyl ammonium salts are reported ranging from almost saturated solutions to very dilute solutions. 6 concentrations each for $(\text{CH}_3)_4\text{NI}$, $(\text{C}_2\text{H}_5)_4\text{NI}$, 7 concentrations for $(\text{C}_3\text{H}_7)_4\text{NI}$ and 2 concentrations for $(\text{C}_4\text{H}_9)_4\text{NI}$.

The charge density and surface excesses are reported for all the solutions. Using certain assumptions, the components of the specifically adsorbed charge are obtained and reported in tabular form. It is shown that the cation is specifically adsorbed and the adsorption increases as we go from tetra Methyl to tetra Ethyl to tetra Propyl salts. The specific adsorption of the cation for these tetra salts is shown to increase with increasing concentration.

On the anodic side it is shown that there is simultaneous specific adsorption of cations and anions. From the evidence gathered from the differential capacity data, it is shown that the cations are not specifically adsorbed on the Mercury surface but on to specifically adsorbed anions. These anions thus form bridges between the cations and the Mercury surface. The existence of bridges has been postulated by FRUMKIN for the cathodic reduction of certain anions. The evidence adduced here shows for the first time the existence of 'Anionic bridges'. The entire capacity curve is explained on a semi-quantitative basis and the structure of the electrical double layer throughout the entire potential range is elucidated.