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ADSORPTION OF SODIUM SALTS OF CITRIC AND PHOSPHORIC
ACIDS AT THE MERCURY ELECTRODE

by

George James Donaldson, B.Eng., M.Sc.

A thesis submitted to the Faculty of
Graduate Studies in partial fulfilment
of the requirements for the degree of
Doctor of Philosophy

Department of Chemistry
Carleton University
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The undersigned recommend to the Faculty
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submitted by George James Donaldson, B.Eng.,
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ABSTRACT

Experimental investigations into electrochemical adsorption at the mercury electrode solution interface were carried out for the sodium salts of orthophosphoric and citric acids. Primary double layer results were obtained by measuring the differential capacitance, interfacial tension and potential of zero charge (p.z.c.) of the mercury-electrolyte solution interface. Capacitance curves at a hanging mercury drop electrode were recorded as a continuous function of the electrode potential using an improved version of an instrument first described by Kowalski and Srzednicki^{68,69}. A modern Lippmann capillary electrometer was employed for interfacial tension measurements and the streaming mercury electrode method gave accurate p.z.c. results for all solutions investigated. Capacitance curves were integrated twice and compared with directly measured interfacial tension data. The primary thermodynamic data were analyzed with the aid of computer programming techniques to obtain the ionic relative surface excess at constant integral values of electrode charge. The diffuse layer theory of Gouy, Chapman and Stern was applied to thermodynamically derived results to calculate the amount of specifically adsorbed charge.

The potential of a sodium ion responsive electrode was measured for all solutions studied in the present work to adjust electrode potentials to the thermodynamic sodium ion potential scale for analysis of double layer results. The sodium ion electrode was found to be of considerable value for investigating changes in

sodium ion activity resulting from the formation of ion-pairs in sodium-citrate solutions. Ancillary information to assist the interpretation of ionic adsorption in the double layer was obtained largely from viscosity and density measurements. Viscosity A and B coefficients were calculated by the Jones-Dole equation. These results were used in conjunction with various other physico-chemical properties to gain an insight into the nature and degree of structure-ordering caused by the different ionic entities in the bulk solution. Attention was also directed towards consideration of acid-base equilibria in aqueous solutions and the possible ionic species present depending on pH and concentration of solute.

The experimental work on phosphates was confined to Na_2HPO_4 and Na_3PO_4 and the results derived from capacitance data were compared with those reported for NaH_2PO_4 by Parsons and Zobel²². Interfacial tension results for Na_3PO_4 were found to be unreliable due to experimental difficulties encountered at polarizations on the anodic side of the p.z.c. Analysis of results for Na_2HPO_4 and Na_3PO_4 showed that anion specific adsorption was absent for electrode charges, $q_m < 0$. Anodic polarization of mercury was found to be restricted to about 6 to 8 $\mu\text{C cm}^{-2}$ of electrode charge and therefore a very limited amount of data was obtained for anion specific adsorption for $q_m > 0$. The order of increasing specific adsorption for positively charged mercury was estimated as: $\text{PO}_4^{3-} < \text{HPO}_4^{2-} < \text{H}_2\text{PO}_4^-$. Experimental problems with interfacial tension measurements and the steeply rising anodic capacitance were attributed to a very rapid increase in anion specific adsorption, eventually leading to the formation of highly insoluble mercury compounds

such as: $(\text{Hg}_2)_3(\text{PO}_4)_2$, Hg_2HPO_4 and HgO . The absence of a hump in the capacitance curves for Na_2HPO_4 and Na_3PO_4 was discussed in terms of strong interactions between water and phosphate ions which severely restricted the freedom of water to reorient under influence of the electrode field.

Specific adsorption from citrate salt solutions was found to increase in the sequence: $\text{Cit}^{3-} < \text{HCit}^{2-} < \text{H}_2\text{Cit}^-$. For disodium citrate solutions specifically adsorbed charge calculations could only be interpreted on a qualitative basis owing to uncertainties about diffuse layer results for complicated mixtures of anions present in solution. Detailed analysis for Na_3Cit solutions showed that the specifically adsorbed anion charge went through a peak value near $q_m \approx 8 \mu\text{C cm}^{-2}$. These results offered direct experimental verification of the correctness of a recent theory proposed by Jenard and Hurwitz⁶² in which field-assisted dissociation was suggested to be followed by ionic association at larger electrical field strength in the double layer. Thus in solutions of trisodium citrate, ion-pairs (NaCit^{2-}) are dissociated near the outer Helmholtz plane (OHP), but at more positive electrode charge where the field at the OHP is large (eg. $10^7 \text{ volt cm}^{-1}$) association was found to occur according to the theoretical predictions of Jenard and Hurwitz. For the citrate system it was experimentally verified that water structure enforced ion-pairing in the bulk solution and in the double layer provided the necessary conditions to support the requirements of the Jenard and Hurwitz theory.

The behavior of adsorbed citrate and phosphate ions was discussed in relation to other ions of more or less structure

ordering influence on the solvent structure. While citrates and phosphates have a comparable effect on the perturbation of the water structure in homogeneous solutions, their different properties observed in the double layer were accounted for by dissimilarities in ionic size and nature of charge distribution. Hydrogen bonding, localized hydrolysis, orientation of solvent and adions were explained in terms of a novel molecular model of the interphase for the adsorption results obtained.

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TABLE OF CONTENTS

ABSTRACT	i
ACKNOWLEDGMENTS	v
TABLE OF CONTENTS	vi
LIST OF FIGURES	x
LIST OF TABLES	xiii

I INTRODUCTION

A. Research Aims	1
B. Nature of Electrode-Solution Interface	2
C. Double Layer Models	
1. Development of a Model	5
2. The Diffuse Layer	8
3. The Inner Layer	9
D. Thermodynamics of the Ideally Polarized Electrode	
1. The Electrocapillary Equation	11
2. The Lippmann Equation	14
3. Relative Surface Excess	17
4. Capacitance of the Double Layer	20
E. Application of Diffuse Layer Theory to Unsymmetrical Electrolytes	
1. Diffuse Layer Charge	21
2. Diffuse Layer Capacitance	25
3. Calculation of Specifically Adsorbed Charge	27
4. Validity of the Gouy-Chapman-Stern Theory	28

II	LITERATURE SURVEY	
A.	Adsorption Studies	29
B.	Viscosity and Structural Properties	37
C.	Ion-Association in Solution and in the Double Layer	44
III	EXPERIMENTAL	
A.	Methods of Studying Adsorption at Charged Interfaces	58
B.	Electrocapillary Measurements	59
C.	Differential Capacitance Measurements	
1.	Basic Principles	62
2.	Capacitance Recording Apparatus	63
3.	Calibration	65
4.	Procedure	66
D.	Auxiliary Measurements	
1.	Streaming Potentials	67
2.	Sodium Ion Electrode Potential	69
3.	Viscosity and Density Measurements	69
4.	Measurement of pH	71
5.	Voltammetry	71
E.	Apparatus	
1.	Electrochemical Cells	72
2.	Electrodes	74
	(a) Saturated Calomel Electrode	
	(b) Hanging Mercury Drop Electrode	
	(c) Drop Delivery System	

E. 3. Chemical Reagents and Other Materials	79
(a) Water Purification	
(b) Mercury	
(c) Electrolyte Solutions	
(d) Nitrogen Gas	
(e) Glassware	
F. Computational Methods	83
IV RESULTS	
A. Reliability of Double Layer Data	
1. Capacitance Curves	85
2. Electrocapillary Curves	88
3. Double Layer Results	88
B. Results of Viscosity Studies	88
C. Results of Density Measurements	95
V DOUBLE LAYER STUDY OF PHOSPHATE SOLUTIONS	
A. Results of Double Layer Studies	99
B. Morphology of Capacitance Curves	103
C. The Capacitance Hump	111
D. Comparison of Electrocapillary and Capacitance Results	114
E. Anion Adsorption at the Uncharged Electrode	116
F. Anion Adsorption at Positively Charged Mercury	117
G. Adsorbed Water and Specific Adsorption	128

VI	DOUBLE LAYER STUDY OF CITRATE SOLUTIONS	
A.	Introductory Remarks	139
B.	Homogeneous Properties of Citrate Salt Solutions	
1.	pH Dependence of Ionic Species	140
2.	Ion-Association in Citrate Solutions	143
3.	Size of Cit^{3-} Anion	147
4.	Structure-Ordering by Citrate Ions	152
C.	Preliminary Double Layer Measurements	154
D.	Disodium Citrate	162
E.	Trisodium Citrate	
1.	Primary Double Layer Results	172
2.	Anion Specific Adsorption	175
3.	Association Effects in the Double Layer	187
4.	Proposed Model and Supplementary Work	192
VII	SUMMARY	201
VIII	REFERENCES	207

LIST OF FIGURES

1. Models of the Electrical Double Layer	7
2. Typical Electrical Double Layer Curves for Interfacial Tension, Electrode Charge and Differential Capacitance at Mercury	16
3. Calculated Curves for q^d/A versus ϕ_2 According to the Gouy-Chapman-Stern theory	26
4. Thickness of the Inner Layer as a Function of Electrode Charge	31
5. States of Ion-Pair Formation	43
6. Variation of the Ion-Pair Dissociation Constant with Electrical Field Strength	54
7. Schematic Diagram of the Capillary Electrometer	60
8. Schematic Diagram of the Automatic Capacitance Recording Apparatus	64
9. Schematic Diagram of the Electrochemical Cell for Capacitance Measurements	73
10. Mercury Drop Delivery System	77
11. Capacitance Curves for 0.05M K_2SO_4	86
12. Capacitance Curves for 0.10M $Na_3Cit.$	87
13. Plot of Jones-Dole Equation for $Li_3Cit.$, $Na_3Cit.$ and $K_3Cit.$	89
14. Plot of Jones-Dole Equation for Sodium-Citrate Salts of Various pH	92
15. Plot of Jones-Dole Equation for NaH_2PO_4 , Na_2HPO_4 and Na_3PO_4	94
16. Temperature Variation of Viscosity for 0.10M $Na_3Cit.$	96
17. Capacitance Curves for Na_2HPO_4 Solutions	104
18. Capacitance Curves for Na_3PO_4 Solutions	105
19. Capacitance Curves for 0.1M NaOH, 0.1M NaH_2PO_4 , 0.04M Na_2HPO_4 and 0.02M Na_3PO_4	107
20. Logarithmic Concentration Diagram for 0.1M Phosphate Solutions	110
21. Anodic Part of Capacitance Curves for Na_2SO_4 with Added NaOH	112

22.	Reciprocal Capacitance as a Function of Reciprocal Diffuse Layer Capacitance for Na_2HPO_4 and Na_3PO_4 Solutions	119
23.	Anion Relative Surface Excess versus Electrode Charge for Na_2HPO_4	121
24.	Anion Relative Surface Excess versus Electrode Charge for Na_3PO_4	122
25.	Anion Relative Surface Excess versus Electrode Charge for NaH_2PO_4	123
26.	Anion Relative Surface Excess versus Electrode Charge for 0.1M Solutions of Na_2SO_4 , NaH_2PO_4 , Na_2HPO_4 and Na_3PO_4	125
27.	Anion Specifically Adsorbed Charge versus Electrode Charge for Na_2HPO_4 and Na_3PO_4	127
28.	Surface Excess of Water versus Electrode Charge for Different Concentrations of Na_2SO_4 and Na_3PO_4	130
29.	Anion Specifically Adsorbed Charge (corrected for adsorbed water) versus Electrode Charge for NaH_2PO_4 , Na_2HPO_4 and Na_3PO_4	134
30.	Schematic Diagram for Adsorbed PO_4^{3-} at a Mercury Electrode	138
31.	Ionic Composition--pH Curves for 0.1M Citrate Solutions	142
32.	Plot of Number of Sodium Ions per Citrate Anion as a Function of Solution pH	145
33.	Ion-Pair Formation Constant versus Coulombic Energy Term for Alkali Metal Citrates	146
34.	Apparent and Partial Molal Volume versus $c^{1/2}$ for $\text{Li}_3\text{Cit.}$	149
35.	Viscosity B-Coefficient versus Partial Molal Volume for some Carboxyl Anions	155
36.	Anodic Part of Capacitance Curves for Constant Ionic Strength Mixtures of Na_2SO_4 and $\text{Na}_3\text{Cit.}$	157
37.	Capacitance Curves for 0.10M Na_2SO_4 with 0.05M Citrate at Different pH Values	159
38.	Capacitance Curves for 0.10M Sodium-Citrate Solutions at Different pH Values	160
39.	Capacitance Curves for $\text{Na}_2\text{HCit.}$, Variable pH Study	165
40.	Capacitance Curves for $\text{Na}_2\text{HCit.}$, Constant pH Study	166

41. Anion Specifically Adsorbed Charge versus Electrode Charge for $\text{Na}_2\text{HCit.}$, Variable pH Study	169
42. Anion Specifically Adsorbed Charge versus Electrode Charge for $\text{Na}_2\text{HCit.}$, Constant pH Study	170
43. Capacitance Curves for $\text{Na}_3\text{Cit.}$ Solutions	173
44. Comparison of Directly Measured Interfacial Tension and Data Obtained by Double-Integration of Capacitance Curves as a Function of Electrode Potential for $\text{Na}_3\text{Cit.}$	176
45. Anion Specifically Adsorbed Charge versus Electrode Charge for $\text{Na}_3\text{Cit.}$	179
46. Calculated Potential Drop Across the Inner Layer versus Amount of Specifically Adsorbed Charge for $\text{Na}_3\text{Cit.}$ at Different Values of the Electrode Charge	181
47. Capacitance Due to Specifically Adsorbed Charge versus Electrode Charge for $\text{Na}_3\text{Cit.}$	183
48. Esin-Markov Plot, ($E_{\pm}$ vs. $\ln a_{\pm}$), for $\text{Na}_3\text{Cit.}$ at Different Values of Electrode Charge	185
49. Esin-Markov Coefficient versus Electrode Charge for $\text{Na}_3\text{Cit.}$	186
50. Anion Specifically Adsorbed Charge versus Electrode Charge; Comparison for 1.00M Sodium- citrate Solutions of Different pH	191
51. Schematic Diagram for Adsorbed Cit^{3-} at a Mercury Electrode	193
52. Comparison of Capacitance Curves for 0.1M Solutions of $\text{Li}_3\text{Cit.}$, $\text{Na}_3\text{Cit.}$, $\text{K}_3\text{Cit.}$ and $(\text{NH}_4)_3\text{Cit.}$	195
53. Comparison of Capacitance Curves for 0.1M Solutions of $\text{Na}_3\text{Cit.}$ and $\text{Na}_3\text{Tricarballylate}$	197
54. Capacitance Curve Typical of Results Obtained for MgSO_4 Solutions	199

LIST OF TABLES

I	Results of Viscosity Measurements at 25°C for Alkali Metal Citrate Salts	91
II	Results of Viscosity Measurements at 25°C for Sodium - Citrate Solutions at Different pH	93
III	Constants of Equation (52) for Citrate Salts at 25°C	97
IV	Double Layer Parameters for Na_2HPO_4	101
V	Double Layer Parameters for Na_3PO_4	102
VI	Ionic Composition of 0.1M Sodium - Phosphate Solutions	109a
VII	Apparent Effect of Hydroxyl Ion Concentration on the Capacitance Hump	113a
VIII	Partial Molal Volume Results for Li_3Cit , Na_3Cit and K_3Cit	150
IX	Double Layer Parameters for Na_2HCit , "Variable pH Study"	163
X	Double Layer Parameters for Na_2HCit , "Constant pH Study"	164
XI	Double Layer Parameters for Na_3Cit	174

CHAPTER I

INTRODUCTION

A. Research Aims

The principal aim of this thesis has been to carry out an experimental investigation of the adsorption behavior on a mercury electrode of certain unsymmetrical electrolytes and to correlate their homogeneous and heterogeneous electrochemical properties. Sodium salts of citric acid and orthophosphoric acid were chosen as the systems of main interest primarily in relation to a general concern regarding the practical aspects of their surface activity. In recent years the widespread use of phosphates by detergent manufacturers has led to some anxiety on the part of the public, government and scientists, because of the possible harm caused to the overall biological balance in lakes, rivers and oceans which has been related to the prolonged use of such compounds¹²³. As a substitute for phosphate additives, nitrilotriacetate (NTA) has been introduced, but with perhaps more deleterious effects, due to the toxicity of its heavy metal chelates. The quest for less objectionable substitutes has led to a suggestion of employing citrates or silicates as builders in commercial detergents, or perhaps even a return to a more rigidly controlled use of the non-toxic phosphates¹.

With the above considerations in mind it was decided to carry out a study of the interfacial and homogeneous solution properties of phosphates and citrates. Electrochemical techniques are convenient for such work, because they provide a direct method of measuring the adsorption (ie. surface activity) of ionic and neutral molecular substances. Such information provides valuable

guidelines for those involved in solving the practical problems related to purification, prevention of pollution and other environmental topics.

To the electrochemist, the salts of orthophosphoric and citric acids offer a challenging problem due to the complexity of applying the methods and theories of the electrical double layer to unsymmetrical electrolytes. There are also the complicated acid-base equilibria to be considered. Finally, it is important to note that relatively less attention has been focussed in the literature on the possible influence that bulk properties of solutions might have on the behavior of ions in the electrical double layer^{2,109}.

In this dissertation therefore, some considerable regard is given to the aspects of structure in the solution bulk phase and their implications in the structural characteristics of electrified interphases.

B. Nature of Electrode-Solution Interface

When an electrode is introduced into an electrolyte solution it perturbs the normal distribution of ions and solvent molecules. This redistribution is manifested by the formation of an electrical double layer (e.d.l.). Several phenomena can result from the reorganization of ionic and molecular species in the solution:

- (i) a net charge transfer may take place across the interface,
- (ii) ions may be attracted to, or repelled from the interface; not necessarily in proportions equivalent to

either their charge or abundance in the bulk of the solution phase,

- (iii) dipolar solvent molecules could be adsorbed and oriented in the electrical field
- and (iv) polarizable ions and molecules may experience deformation in the non-isotropic electrical force field of the interphase.

Since any combination of these effects is possible, the interphase may consist of more than one distinct layer. However, the term, electrical double layer, has been retained as a general description of what is actually an electrical multilayer in many instances.

Frequently throughout the text, the terms "interface" and "interphase" will be deliberately employed to discriminate different parts of the e.d.l. The "interphase" is the three-dimensional region between the bulk of the electrode phase and the bulk of the electrolyte phase in which there is a more or less gradual change in local concentrations and other properties arising on account of adsorption. The term "interface" is used to describe the two-dimensional electrode surface in contact with the solution. The electrical field referred to above results from the superimposition of the electrode field and that due to ions in the interphase. Solvent molecules therefore come under either a conflicting or reinforcing influence of the fields arising both at the interface and locally at ions in the double layer.

A major contribution to present knowledge about the structure of the e.d.l. comes from studying the mercury electrode in aqueous

electrolytes. The popular choice of mercury as an electrode material follows from the fact that it can be easily purified¹²⁷ and, being a liquid, its real surface area is known to a precision not yet attainable for solid metals. In this respect solid electrodes suffer from such undesirable properties as porosity, surface defects and mechanical strain. In addition, mercury is almost unique by virtue of its low chemical reactivity and large hydrogen overvoltage. This latter characteristic makes it possible to work at applied electrical potentials, which in the case of most other metals would result in the rapid evolution of hydrogen gas due to electrolysis of the solvent. Since at normal ambient temperatures mercury is a liquid, its interfacial tension is readily measured as a function of the applied electrical potential. Such measurements lend themselves to thermodynamic analysis, and will be described below.

In this thesis, exclusive use has been made of the mercury electrode, operating in the range of applied potentials in which it is an "ideally polarized" electrode. By definition, an ideally polarized electrode is

"....a system composed of a metal in contact with an electrolyte solution for which, at equilibrium, the concentration of every charged component is finite in one phase only".³

As a corollary to this it can be stated that when the potential difference between the electrode and the solution is altered slightly, from an external polarizing source, no finite amount of charge must cross the metal-solution interface. Experimentally, the ideally polarized mercury electrode behaves like an electrical condenser without leakage. The capacitance of the mercury-electrolyte

interphase can be measured to a high degree of accuracy, and like the interfacial tension, is susceptible to thermodynamic analysis. Thermal, mechanical and chemical equilibrium are assumed to prevail at the ideally polarized mercury electrode. The thesis will therefore not be concerned with charge transfer in the e.d.l. and will employ equilibrium thermodynamic methods to analyze the experimental data.

C. Double Layer Models

1. Development of a Model

The earliest models for the e.d.l. were proposed by Helmholtz⁴ and Quincke⁵ in the middle of the last century. A planar array of ions of charge opposite to that of the electrode was assumed to form in the solution phase (see figure 1a). Independently, Gouy^{6,7} and Chapman⁸ introduced a significant modification of the Helmholtz model by considering the effect of thermal motion on the array of electrostatically attracted ions; this is shown schematically in figure(1b). Their approaches had the same mathematical foundations as the Debye-Huckel theory of ionic activities, but in fact preceded this well-known work by a decade. In the Gouy-Chapman theory ions are treated as point charges in a dielectric continuum and the Boltzmann distribution is invoked to evaluate the ionic population density in terms of the electrostatic work required to move a charge from infinity to a point in the e.d.l. The Gouy-Chapman representation has been revised, but only with respect to details, so that their basic mathematical formulations are still used today. A further improvement of the double layer model was

made by Stern⁹ who suggested that ions were limited to a distance of closest approach to the electrode (figure 1c). With the inclusion of Stern's modification, this version of the double layer model is known as the Gouy-Chapman-Stern theory (GCS).

The most significant, recent contributions to the GCS model were from Grahame³ and Bockris, Devanathan and Muller¹⁰. Their innovations which are shown in figure (1d) and (1e), respectively, incorporate the properties of the e.d.l. essential to the model as it is currently known.

Basically, the e.d.l. consists of three main parts: (a) the electrode phase, and in the solution phase, (b) an inner (or compact) layer only a few Angstroms in thickness, and (c) a diffuse (or outer) layer, extending in three-dimensional space outwards to the bulk of the solution.

The charge on the metallic electrode is controlled indirectly by application of a potential difference between it and a counter electrode. The latter is located at a distance sufficiently large so that there is no overlap of the respective double layers. The density of excess (or deficit) electronic charge on the electrode is given the symbol, q_m , to indicate charge on the metallic phase (m). This quantity can be measured, because it has a well-defined thermodynamic significance, as will be described presently (see section D). The units of q_m are usually given in microcoulombs per unit surface area of the electrode ($\mu\text{C cm}^{-2}$); $q_m < 0$ signifies an excess of electrons on the electrode and $q_m > 0$ a deficiency. Thus positive and negative polarizations correspond to $q_m > 0$ and $q_m < 0$, respectively. It has been the general tendency of many

Figure 1. Models of the electrical double layer according to: (a) Helmholtz, (b) Gouy and Chapman, (c) Stern, (d) Grahame and (e) Bockris, Devanathan and Muller.

authors to use the terms "anodic" and "cathodic" when describing the metallic charge state as $q_m > 0$ and $q_m < 0$, respectively.

2. The Diffuse Layer

The inner boundary of the diffuse layer is located in a plane parallel to the electrode surface, called the outer Helmholtz plane (OHP). In the one-dimensional coordinate system employed, the OHP is at $x = x_2$ (see fig. 1e). The ionic population of the diffuse part of the e.d.l. is accounted for by ordinary electrostatic forces and therefore, the GCS theory is used to calculate the space-charge in this three-dimensional region. The mathematical formulation of the GCS model can be solved in one coordinate only, and the space-charges so calculated are given in the same units as for q_m (ie. $\mu\text{C cm}^{-2}$). The diffuse layer charges are q_+^d and q_-^d for cations and anions, respectively. The net charge of the diffuse layer is given the symbol, q_s^d , where s denotes the solution phase of the e.d.l., and d stands for diffuse layer. If there are no ions between the electrode and the OHP, then by overall electro-neutrality, the electrode charge is equal in magnitude to the net charge in the diffuse layer.

$$-q_m = q_s^d = q_+^d + q_-^d \quad (1)$$

The diffuse layer charge is the excess charge contained in a column of solution of unit cross-section, extending from the OHP all the way into the bulk of the solution phase. Accordingly, diffuse layer ions are not all located in the OHP as depicted by the simple Helmholtz model (figure 1a). Between the OHP and the bulk of the solution there exists an ionic concentration --

distance profile, as well as corresponding profiles for potential, electrical field, solvent concentration, etc. Ions which populate the diffuse layer are said to be non-specifically adsorbed. This is in contrast to the term, "specific" adsorption, which will be defined later. Non-specific adsorption implies ionic adsorption by purely electrostatic forces existing due to the charged metal and the ions in solution. Currently held theories^{10,16,17,126} maintain that many ions (especially small spherical cations) retain their primary hydration under the influence of long-range electrostatic forces operating in the diffuse layer. Furthermore, the closest distance which such ions are believed to come to the electrode is equivalent to their hydrated ionic radii plus the thickness of a monolayer of water dipoles on the surface of the electrode. This model is shown for singly charged cations in figure(1e). The OHP is defined as the charge centre of closest approach for these non-specifically adsorbed cations. Inevitably, complications arise in fixing the position of the OHP when considering the differences in radii of dissimilar ions. This is one of the inherent weaknesses of the GCS theory and also of the Bockris, Devanathan and Muller model¹⁰.

3. The Inner Layer

In many electrolytes, between the OHP and electrode surface adsorbed ions are present as well as solvent molecules. These inner layer ions are said to be specifically adsorbed. They may lose some of their water of hydration, at least in the direction of the electrode surface, and be in physical contact with the

metallic surface. Thus, specifically adsorbed ions are also referred to as being contact adsorbed¹¹. The locus of electrical centres of specifically adsorbed ions defines the inner Helmholtz plane (IHP).

An indication of this type of adsorption is experimental evidence showing that many anions are adsorbed even when the electrode is negatively charged. The halide ions are a good example of specific adsorption, which increases in the order: $F^- < Cl^- < Br^- < I^-$. Small cations, by virtue of the large electrical fields at their surfaces, are strongly hydrated and do not appear to be specifically adsorbed (eg. Li^+ , Na^+ , Mg^{++}). However, Cs^+ has shown evidence of specific adsorption¹², a fact contributing to the widely accepted notion that ionic hydration may be one of the principal factors responsible for adsorption behavior in the e.d.l.^{10,13}.

The term, specific adsorption, suggests that some forces other than electrostatic ones are involved in the adsorption process. One of the commonly used criteria for detection of specific adsorption is to compare experimental results with predictions based on the GCS theory. Specific adsorption is then, all adsorption which cannot be accounted for by this electrostatic model; it is sometimes given the name, superequivalent adsorption¹³. It was suggested by Grahame et al.^{3,14} that covalent bonding of ions with the electrode was responsible for specific adsorption. However, this argument is in direct conflict with the observed trend for the halide ions which has the fluoride ion least specifically adsorbed yet possessing the largest Hg-X bond energy. There is a

much better correlation between ionic hydration for halide ions and their degree of specific adsorption at the mercury electrode¹³. This factor also appears important for the alkali metal cations as indicated above. There may also be a significant influence due to structural effects which different ions have on each other and on the solvent. Specific adsorption may be connected in this way with a tendency for the solvent to reject structure-disordering ions and, in effect, to squeeze them out of the solution phase. The structure-disordering trends for the halides increase from F^- to I^- and for the alkali cations structure-ordering in aqueous solutions decreases from Li^+ to Cs^+ .

D. Thermodynamics of the Ideally Polarized Electrode

1. The Electrocapillary Equation

Over a specified range of applied electrical potential the mercury electrode is ideally polarized and in a state of equilibrium with an electrolyte solution when no electrochemical reaction occurs. The equilibrium condition is defined by specifying the temperature, external pressure, chemical potentials in both the electrode and solution phases, and an additional variable which characterizes the electrical state. This may be either the charge on the electrode, q_m , or the potential of the electrode given with respect to a reference electrode. Many excellent articles have been published in which a thorough thermodynamic analysis has been given for the ideally polarized electrode. The author has found the following to have been particularly helpful: Grahame's review³, Parsons' general treatment¹⁵, the excellent book by Delahay¹⁶,

Mohilner's thorough analysis¹⁷ and a graduate level textbook by Bockris and Reddy¹²⁶. A complete thermodynamic treatment will not be presented here, but the fundamental equations will be given for a particular system in order to illustrate those topics which are relevant to the thesis material.

A typical equilibrium system, at constant temperature and pressure, is the cell:

At each electrode copper wires, Cu^I and Cu^{II} are connected to a potentiometer. The interphase is indicated by the symbol σ between the pure phases S (electrolyte solution) and M (mercury electrode). The choice of sodium sulphate was made to direct attention to the special form of equations in the development of double layer theory and to indicate thermodynamic requirements for selecting an appropriate reference electrode. In this case electrodes are available which are reversible to the sodium ion and to the sulphate ion. Certain terms found in the electrocapillary equation depend on the nature of the reference electrode. The final equation is derived from the Gibbs adsorption equation which can be applied to any metal solution interface at equilibrium. At constant temperature and pressure the Gibbs equation has the form:

$$-d\gamma = \sum_i \Gamma_i d\mu_i \quad (2)$$

As applied to the cell above, γ is the interfacial tension at σ , Γ_i is the surface excess of component i per unit area of the

interface and μ_i is its chemical potential. For ions, μ_i must be replaced by the electrochemical potential:

$$\bar{\mu}_i = \mu_i + z_i F \phi_i \quad (3)$$

The electrochemical potential of ionic species i is simply its chemical potential plus the electrical term comprising Faraday's constant F , the ionic valency (with sign), z_i and the inner potential of the phase, ϕ_i . Inner potentials are themselves not measureable¹⁵, but differences in inner potential between different phases are obtained potentiostatically, and it is these which are required in the final analysis.

Equation (2) is applied to the cell by considering the equilibria involved in pure phases M and S , the reference electrode, and electrons at the junctions of the copper leads. Charge neutrality must be maintained in S and q_m is equated with the net charge developed in the e.d.l., q_s (ie. $-q_m = q_s$). Components of the phases are related through the Gibbs-Duhem equation, resulting in transformation of equation (2) into the following:

$$-d\gamma = q_m dE_+ + \Gamma_{-(w)} d\mu_{salt} \quad (4)$$

$$\text{or} \quad -d\gamma = q_m dE_- + \frac{\Gamma_{+(w)}}{2} d\mu_{salt} \quad (4a)$$

The cell potential differences, E_+ and E_- , specify measurement against a cation or anion reversible reference electrode, respectively. In equations (4) and (4a), μ_{salt} is the chemical potential of the aqueous salt solution and the denominator 2 in (4a) results from the formation of two sodium ions from dissociation of one molecule of Na_2SO_4 . The relative surface excesses of anions and cations in the e.d.l. are $\Gamma_{-(w)}$ and $\Gamma_{+(w)}$, respectively. These are

related to the surface excesses of equation (2) and the surface excess of the reference component (water in this case, indicated by $\Gamma_{(w)}$) through the identities:

$$\Gamma_{-(w)} = \Gamma_- - \frac{x_{\text{salt}}}{x_w} \Gamma_w \quad (5)$$

$$\text{and } \Gamma_{+(w)} = \Gamma_+ - \frac{2x_{\text{salt}}}{x_w} \Gamma_w \quad (5a)$$

The mole fractions of salt and of water are x_{salt} and x_w , respectively. Equations (4) and (4a) are the electrocapillary formulae for the equilibrium interfacial system considered here. Several other important relationships can be derived from them and some will be discussed below. More generalized expressions may be found in the review articles mentioned previously^{3,15,16,17,126}.

2. The Lippmann Equation

In general, equations (4) and (4a) may be combined for any $z - z'$ (unsymmetrical) electrolyte:

$$-d\gamma = q_m dE_{\pm} + \frac{\Gamma_{\mp(w)}}{\nu_{\mp}} d\mu_{\text{salt}} \quad (6)$$

where $\nu_{\mp}$ is the number of anions (negative sign) or cations (positive sign) resulting from ionization of the salt. From (6) it follows that the charge on the metal is given, at constant temperature, (T), pressure (P) and chemical potential of all components by:

$$q_m = - \left(\frac{\partial \gamma}{\partial E} \right)_{T, P, \mu_i} \quad (7)$$

This is the Lippmann equation. The subscript on E has been dropped

since it does not matter which reference electrode type is used. The electrode charge is thus a thermodynamic quantity which can be obtained by differentiation of the electrocapillary curve (ie. a γ vs. E plot). Such curves are almost parabolic in shape. A typical electrocapillary curve and its corresponding charge curve are shown in figure (2). The apex of the γ vs. E curve is called the electrocapillary maximum (e.c.m.). It corresponds to a net cancellation of charge on the solution side of the interface. The potential of the e.c.m. is often referred to as the potential of zero charge (p.z.c.). At potentials more positive than the e.c.m. ($E = E_z$ at the e.c.m.) anions are attracted by the positive electrode charge. Cations are attracted at electrode potentials negative to E_z . The coordinates of the e.c.m. (ie. E_z and the interfacial tension maximum ($\gamma^{\max}$)) are of particular interest on a comparative basis for different electrolytes and also for variations of concentration for any one solute. For comparing effects due to concentration changes the values of E_z should be expressed on a scale referred to a reference electrode of constant activity. This is to avoid contributions to E_z caused by ion activity changes, as given by the Nernst equation. It has been found that E_z is essentially the same, regardless of the nature and concentration, for some solutes, whereas for others, E_z changes appreciably^{3,16}. Specific adsorption of ions causes E_z to shift as a function of concentration; towards more negative values for increased anion specific adsorption, and in the opposite direction for cations. This serves as another criterion for detecting specific adsorption, however, E_z could presumably not vary in the case of simultaneous

Figure 2. Typical double layer curves for: interfacial tension (γ), electrode charge (q_m) and differential capacitance (C). Potentials are with respect to the n.z.c. Data for 0.1M trisodium citrate.

specific adsorption of both positive and negative ions.

3. Relative Surface Excess

The relative surface excess is obtained from variations of the interfacial tension as a function of chemical potential; temperature, pressure and electrical potential (ie. E_+ or E_-) remaining constant.

$$\Gamma_{\pm(w)} = -v_{\pm} \left(\frac{\partial \gamma}{\partial \mu_{\text{salt}}} \right)_{T, P, E_{\mp}} \quad (8)$$

Note, that to calculate $\Gamma_{-(w)}$ the partial derivative in equation (8) is evaluated at constant E_+ ; this stipulates the requirement of obtaining cell potentials fixed to the activity of one of the ionic species in solution. It is to be understood in equation (8) that all chemical potentials (ie. activities) must be constant, except that of the species whose relative surface excess is required. From electrocapillary curves q_m can be obtained by equation (7), so when one of the relative surface excesses (say $\Gamma_{-(w)}$) is calculated by equation (8), the other ($\Gamma_{+(w)}$) may be found by difference using (9) and (10):

$$-q_m = q_s = q_- + q_+ \quad (9)$$

The components of charge are q_- and q_+ for total anions and cations, respectively. These are related to their relative surface excesses:

$$q_- = z_- F \Gamma_{-(w)} \quad (10)$$

$$q_+ = z_+ F \Gamma_{+(w)} \quad (10a)$$

The relative surface excess for the salt may be determined by application of equation (8) at $q_m = 0$:

$$\left(\frac{\partial \gamma^{\max}}{\partial \mu_{\text{salt}}} \right)_{T,P,E_z} = - \left(\frac{\Gamma_{\pm}(w)}{v_{\pm}} \right) E_z \equiv -\Gamma_{\text{salt}(w)} \quad (11)$$

Since many salts exhibit a decrease in $\gamma^{\max}$ with increasing concentration, they are adsorbed at the uncharged electrode (ie. $\Gamma_{\text{salt}(w)} > 0$). However, for some electrolytes $\gamma^{\max}$ is constant over a wide range of concentrations, but then increases in very concentrated solution. This suggests a negative relative surface excess of salt^{3,18} and cf 109. In view of equations (5) and (5a), this effect may be due to the larger value attributed to the mole fraction of salt, if the surface excess of salt (ie. Γ_+ or Γ_-) is sufficiently small. Negative values for $\Gamma_{\text{salt}(w)}$ seem to occur for salts whose ions are highly hydrated^{18,29,109}. The hydrophilic nature of the ions thus contributes to very small values for $\Gamma_{\text{salt}(w)}$ and in fact, the surface excess of both ions and salt (at the e.c.m.) may simply be zero. The fundamental problem involved here is the unknown quantity, Γ_w , which is the surface excess of water. This is dealt with below.

Relative surface excesses may be calculated at constant q_m , rather than at constant $E_{\pm}$. This is achieved by a change of variables in the electrocapillary equation. The method was introduced by Parsons who defined a function:

$$\xi_{\pm} = \gamma + q_m E_{\pm} \quad (12)$$

which is known as the "Parsons auxiliary function"¹⁹. Equation (6) can now be written in a new form:

$$d\xi_{\pm} = E_{\pm} dq_m - \frac{\Gamma_{\pm}(w)}{v_{\pm}} d\mu_{\text{salt}} \quad (13)$$

from which the relative surface excess at constant q_m is:

$$\Gamma_{\pm(w)} = -v_{\pm} \left(\frac{\partial \xi_{\pm}}{\partial \mu_{\text{salt}}} \right)_{T,P,q_m} \quad (14)$$

It is important to emphasize that thermodynamic treatment of double layer measurements yields only the relative surface excess. In order to calculate the surface excess (ie. non-relativized, $\Gamma_{\pm}$, see equations 5 and 5a) it is necessary to know not only the bulk solution composition (ie. x_{salt}/x_w), but also the surface excess of water, Γ_w . Knowledge of Γ_w must come from a non-thermodynamic assumption in the form of a model for the e.d.l. In the Gibbs model for an electrode-aqueous solution interface, Γ_w is set to zero at the Gibbs dividing surface. It follows, that the relative surface excess of an ion is equal to its surface excess, if reckoned from the Gibbs dividing surface. However, the location of the Gibbs dividing surface is arbitrary, being defined by $\Gamma_w \equiv 0$. Therefore, thermodynamics can provide only surface excess quantities which are relative to the reference component; in this case water. Models of the e.d.l. cannot identify the location of the Gibbs dividing surface, but only the IHP and OHP in terms of ions and molecules of definite size. Calculations based on the GCS model provide surface excesses which are calculated from the OHP (ie. OHP is used as a reference plane). It follows from this distinction between the OHP and Gibbs dividing surface, that even if specific adsorption does not occur, one cannot expect perfect agreement between measured relative surface excesses (ie. thermodynamic quantities) and values calculated from the GCS model¹⁷. The relative error is given by:

$$\frac{|\Gamma_{\pm}^d - \Gamma_{\pm}(w)|}{|\Gamma_{\pm}^d|}$$

where $\Gamma_{\pm}^d$ is the surface excess calculated from the GCS theory and represents the diffuse layer excess of charge reckoned from the OHP. The magnitude of this relative error will be small when $\Gamma_{\pm}(w)$ is large and when solutions are dilute. However, these are counteracting tendencies, because ionic adsorption generally increases with concentration. The relevance of these considerations will become clearer when the GCS model calculations are presented in section E.

4. Capacitance of the Double Layer

The second derivative of the electrocapillary curve (equation (7)) is defined as the differential capacitance of the double layer, C:

$$C = -\left(\frac{\partial^2 \gamma}{\partial E^2}\right)_{T,P,\mu_{\text{salt}}} = \left(\frac{\partial q_m}{\partial E}\right)_{T,P,\mu_{\text{salt}}} \quad (15)$$

The word capacitance, to be used henceforth, will be understood to mean the differential capacitance, C. This capacitance differs from that of an ordinary capacitor in electrostatic theory, because the double layer charge is not proportional to the electrode potential. This explains why the electrocapillary curve is not a true parabola. The integral, or static capacitance, K is defined in terms of the electrode potential at the e.c.m., E_z :

$$K = \frac{q_m}{E - E_z} \quad (16)$$

Differential and integral capacitances both vary with electrode

potential and are related through q_m :

$$C = K + (E - E_z) \left(\frac{\partial K}{\partial E} \right)_{T,P,\mu_{\text{salt}}} \quad (17)$$

Thus, only at the e.c.m. are K and C equal.

From equation (15) it can be seen that γ may be computed by a double integration of C with respect to E . It is customary, and a convenient practice to choose the e.c.m., where $q_m = 0$ and $\gamma = \gamma^{\text{max}}$, for the integration constants. Since C is the second derivative of γ (see equation (15)), it is more sensitive to small changes in the structure of the e.d.l. than is γ . For this reason capacitance data may be preferred over interfacial tension measurements. However, in the present studies both types of data were obtained in most circumstances as a means of checking on the reliability of experimental measurements²⁰. In figure (2) some double layer data have been plotted to further illustrate the relationships between γ , q_m and C . The capacitance in this case was the experimentally measured function and q_m and γ were obtained by appropriate integration as described above.

E. Application of Diffuse Layer Theory to Unsymmetrical Electrolytes

1. Diffuse Layer Charge

In this section an outline will be given of the formulation of equations required for application of the GCS diffuse layer theory. Several textbooks present this subject in a detailed and critical manner^{15,16,17}, but few authors take the calculations beyond the simplest form for symmetrical electrolytes. In the following presentation the derivations will be outlined according to the

approach taken by Grahame³.

The typical solution is assumed to consist of an unsymmetrical electrolyte dissolved in water. There are v_+ cations and v_- anions formed from ionization of the electrolyte; their valencies are z_+ and z_- , respectively. It is understood from the previous description of the GCS e.d.l. model (see section C) that the region of interest extends from the OHP to the bulk of the solution phase. Distances are expressed in a one co-ordinate reference system; $x = x_2$ locates the OHP at which the electrical potential is designated ϕ_2 . The electrical field strength, $d\phi/dx$ varies with x , and is zero at an infinite distance from the OHP. The dielectric coefficient, ϵ is assumed constant for all $x > x_2$, and is assigned the value for pure water in the absence of an electrical field at 25⁰ ($\epsilon = 78.54$). Considerations regarding the electrical field and ionic concentration dependence of ϵ will be important later in the thesis. For this reason it was preferable to refer in general terms to ϵ as the dielectric "coefficient", rather than the dielectric "constant".

At any point in the diffuse layer Poisson's equation is:

$$\frac{d^2\phi}{dx^2} = - \frac{4\pi\rho}{\epsilon} \quad (18)$$

Here, ρ is the electrical charge density per unit volume at a point at which the potential is ϕ . Ions in the diffuse layer are in equilibrium with those in the bulk, so from equality of electrochemical potentials (equation (3)) a Boltzmann distribution may be written for the concentration of ions of type i (C_i) at any point x :

$$C_i = C_i^0 \exp\left(- \frac{z_i F\phi}{RT}\right) \quad (19)$$

The bulk concentration of i is C_i^0 , and it is assumed in arriving at equation (19) that the work done to move ion i from the bulk to point x is simply the electrostatic work term ($z_i F \phi$).

An expression for ρ can be given in terms of equation (19):

$$\rho = \sum_i C_i z_i F = \sum_i z_i F C_i^0 \exp\left(-\frac{z_i F \phi}{RT}\right) \quad (20)$$

Equations (18) and (20) are combined and integrated, noting that $\phi \rightarrow 0$ and $d\phi/dx \rightarrow 0$ as $x \rightarrow \infty$.

$$\frac{d\phi}{dx} = \pm \left[\frac{8\pi RT}{\epsilon} \sum_i C_i^0 \left\{ \exp\left(-\frac{z_i F \phi}{RT}\right) - 1 \right\} \right]^{1/2} \quad (21)$$

Gauss' theorem gives the excess charge per unit area in a plane normal to x :

$$\frac{\epsilon}{4\pi} \left(\frac{d\phi}{dx} \right)_{x_2} = q^d \quad (22)$$

By combining equations (21) and (22), and evaluating $d\phi/dx$ at x_2 , an expression is obtained for the excess charge in the diffuse layer.

$$q^d = \pm \left[\frac{\epsilon RT}{2\pi} \sum_i C_i^0 \left\{ \exp\left(-\frac{z_i F \phi_2}{RT}\right) - 1 \right\} \right]^{1/2} \quad (23)$$

The signs in equations (21) and (23) are taken such that q^d is of opposite sign to ϕ_2 . That is, an abundance of cations is present in the diffuse layer when the potential at the OHP is negative; and vice versa for anions. Equation (23) gives the total diffuse layer excess charge per unit area of the interface, in a column of solution which extends from the OHP to the bulk of the solution phase. Recalling the discussion of section D.3, q^d is said to be reckoned from the OHP.

For a 1:1 electrolyte equation (23) takes a simple form:

$$q^d = + 2A \sinh(y/2) \quad (24)$$

$$\text{where } A = \left(\frac{RT\epsilon C^0}{2\pi} \right)^{1/2} \text{ and } y = |z| F \phi_2 \frac{2}{RT}$$

The expressions in A and y occur again in more complicated formulae below.

It is now worthwhile to enquire how much of the excess charge, q^d , is attributable to an excess or deficiency of cations and how much to anions in the diffuse layer. The component parts of q^d are taken as q_+^d for cations, and q_-^d for anions, and are defined by equations analogous to those given above.

$$q_+^d = \int_{x_2}^{\infty} (\rho_+ - C_+^0 z_+ F) dx$$

$$q_-^d = \int_{x_2}^{\infty} (\rho_- - C_-^0 z_- F) dx$$

Separate Boltzmann expressions can be written for ρ_+ and ρ_- , the volume charge densities for cations and anions, respectively, analogous to equation (20). For a 1:2 electrolyte (eg. Na_2SO_4) the following charge components are obtained:

$$q^d = A \left[\exp(2y) + 2 \exp(-y) - 3 \right]^{1/2} \quad (25a)$$

$$q_+^d = A \left[(1 + 2 \exp(-y))^{1/2} - \sqrt{3} \right] \quad (25b)$$

$$q_-^d = -A \left[\sqrt{3} - \exp(y) \left[1 + 2 \exp(-y) \right]^{1/2} \right] \quad (25c)$$

In the case of 1:3 electrolytes (eg. Na_3PO_4) the integrals are

not easily simplified, but can be evaluated by numerical methods or graphical integration. The formulae used for 1:3 electrolytes²¹ in this thesis are:

$$q^d = A \left[3 \exp(-y) + \exp(3y) - 4 \right]^{1/2} \quad (26a)$$

$$q_+^d = \frac{3A}{2} \int_{y_2}^0 f(y+) dy \quad (26b)$$

$$q_-^d = -\frac{3A}{2} \int_{y_2}^0 f(y-) dy \quad (26c)$$

There, the integration limit $y_2 = \frac{F\phi_2}{RT}$ and the functions are:

$$f(y+) = \frac{A (\exp(-y) - 1)}{q^d} \quad (27a)$$

$$f(y-) = \frac{A (\exp(3y) - 1)}{q^d} \quad (27b)$$

In figure (3) representative curves have been drawn for 1:1, 1:2 and 1:3 electrolyte types. These data are meant to illustrate the dependence of q_-^d on the anion valency as a function of ϕ_2 . The simple GCS theory was used as described above, but the concentration variable was eliminated from consideration by plotting q_-^d/A rather than q_-^d .

2. Diffuse Layer Capacitance

The capacitance of the diffuse layer was defined by Grahame²¹ as $C^d = \frac{dq^d}{d\phi_2}$. He reported general equations for electrolytes of the type $m:1$.

$$C^d = A \left(\frac{Fm}{2RT\sqrt{I'}} \right) \frac{(\exp(my) - \exp(-ly))}{[m \exp(-ly) + 1 \exp(my) + (m+1)]^{1/2}} \quad (28)$$

Figure 3. Anion charge in the diffuse layer (q_d^-) as a function of potential at the outer Helmholtz plane (ϕ_2).

For a 1:3 electrolyte $m = 1$, $l = 3$ and $l' = 1$.

3. Calculation of Specifically Adsorbed Charge

The method will be given for calculating the charge due to specifically adsorbed anions, q'_- . It is assumed that experimental data are available as values of anion relative surface excesses ($\Gamma_{-(w)}$) for various q_m and a particular solution concentration. Corresponding relative surface excesses for cations ($\Gamma_{+(w)}$) are easily calculated by equations (9) and (10) as discussed in section D.3. It is customary to assume no specific adsorption of cations when $q_m > 0$, which amounts to setting $z_+ \Gamma_{+(w)}$ equal to q_+^d . Since the GCS theory gives q_+^d as a function of ϕ_2 , one now may obtain a value of ϕ_2 corresponding to the experimental values: $\Gamma_{+(w)}$ and $\Gamma_{-(w)}$ at a specified q_m . Then, using this value of ϕ_2 , the GCS calculation is done to obtain a corresponding value of q_-^d , the charge due to anions in the diffuse layer. Finally, the charge due to specifically adsorbed anions is calculated thus:

$$q'_- = z_- \Gamma_{-(w)} - q_-^d \quad (29)$$

where q'_- can now be identified with a particular electrode charge and OHP potential.

To calculate cation specific adsorption an analogous procedure may be followed, assuming first that the anion is not specifically adsorbed. The validity of this assumption depends on the electrode charge and in particular on the nature of the negative ion, since anions tend to exhibit stronger specific adsorption properties than simple cations such as Li^+ , Na^+ , K^+ .

4. Validity of the Gouy-Chapman-Stern Theory

The GCS theory is an over-simplified representation of the diffuse part of the e.d.l. Its weaknesses are similar to those incorporated into the Debye-Huckel theory of electrolyte solutions, however it has served as a reliable first approximation even in relatively concentrated solutions. One reason for its relative success is that it does not linearize the Poisson-Boltzmann equation as does the Debye-Huckel theory. Some of the more obvious defects in the GCS model should be mentioned. It treats ions as point charges in a dielectric continuum of fixed dielectric coefficient; both concepts being opposed to current understanding about aqueous electrolyte solutions. Activity coefficients are neglected as are dielectric saturation and polarizability of ions and solvent. The OHP is assumed to be at the same distance from the electrode, regardless of the size, charge distribution and shape of the various ionic species. No account is taken of incomplete dissociation of solute or ion-pair formation. Despite these imperfections, the diffuse layer theory of Gouy, Chapman and Stern continues to be a convenient one by which reasonably reliable double layer data can be analyzed and adsorption properties obtained. It has been applied with success in the treatment of the diffuse layer even in the case of relatively concentrated electrolytes in excess of 1M.

CHAPTER IILITERATURE REVIEWA. Adsorption Studies

This chapter is a review of recent literature on the e.d.l. and homogeneous electrolyte properties which have a direct bearing on the interpretation of adsorption processes at the electrode-solution interface. Relatively few papers have been published on double layer work for aqueous phosphate electrolytes, and no quantitative information exists for citrate salts. However, the literature abounds with studies of electrochemical adsorption of organic compounds and symmetrical inorganic electrolytes, only a few of which are directly related to the solutes being investigated in the present work.

Parsons and Zobel²² examined the interphase between mercury and aqueous sodium dihydrogen phosphate (NaH_2PO_4). Anion specific adsorption was practically non-existent at negative and zero electrode charges, but increased greatly on a positively charged electrode. Results reported in this work were obtained up to $q_m \approx 20 \mu\text{C cm}^{-2}$. The authors stressed the difficulty of making comparisons between measured anion (relative) surface excesses and those obtained from the GCS theory when very weak specific adsorption occurs. In highly concentrated solutions this difficulty is due inter alia to the unknown variability of the dielectric coefficient and the surface excess of water, as discussed previously in section I-D. Inaccuracies occur in dilute solutions of weakly adsorbed ions, because the relative surface excess charge (q_-) often is smaller in magnitude than the charge on the electrode (q_m). In addition, experimental problems with dilute solutions were reported.

Parsons and Zobel used their experimental results for the weakly adsorbed NaH_2PO_4 to calculate the thickness of the inner part of the e.d.l.²². The basis of this calculation is that discrepancies between the surface excess obtained by the GCS theory and that calculated by fixing the Gibbs dividing surface to correspond to zero adsorption of water, is probably due to the presence of an ion-free layer of water adjacent to the electrode surface^{22,108}. In figure(4) Parsons and Zobel's²² calculations are reproduced, showing the ion-free layer thickness as a function of q_m . They suggested that the maximum value at $q_m = -6\mu\text{C cm}^{-2}$ was significant in that it corresponded to the region of electrode charge in which the density of water molecules in the inner layer and the dielectric coefficient pass through a minimum. This is also where a cathodic minimum occurs in the capacitance curve. This paper by Parsons and Zobel has become established as a model for interpreting many other double layer studies. In a subsequent publication²³, the same authors used NaH_2PO_4 as a supporting electrolyte to investigate the adsorption of acetanilide, making use of the fact that H_2PO_4^- ions are specifically adsorbed only on positively charged mercury. Besides the above references, very little additional double layer evidence is available for the phosphate system. From impedance measurements it has been shown that Hg_2HPO_4 forms at 240 mV positive to the SCE potential at a mercury electrode dipping into a phosphate-nitrate buffer solution ($\text{pH} = 6.52$)²⁴. It is of some interest to note that adsorption of H_2PO_4^- ions, on positively charged platinized platinum, was found to be similar to that of sulphate ions²⁵.

Figure 4.

Thickness (x) of the inner layer as a function of electrode charge. (from ref. 22)

The adsorption characteristics of NaOH solutions at mercury are of direct interest to the present work, because Na_3PO_4 solutions are very alkaline. Payne²⁶ studied the mercury-aqueous NaOH interphase and by using GCS diffuse layer theory he concluded that very little anion specific adsorption could be detected. Double layer measurements were restricted to only small positive electrode charges, because the capacitance increased very rapidly with increase in potentials positive to the p.z.c. This sudden increase in capacitance appeared to be asymptotic to the reversible mercuric oxide electrode potential, implying that discharge of OH^- was responsible for this feature of the capacitance curves. It has also been reported that mercury first dissolves rapidly as $\text{Hg}(\text{OH})_2$ during anodic polarization in NaOH, and then a film of HgO is formed on the surface^{27,28}. The steep rise in the capacitance curve at extreme positive potentials is therefore attributed to a rapid increase in adsorption of hydroxyl ions which is followed ultimately by an electrochemical reaction. Recent studies¹²⁸ on platinum electrodes in NaOH also show a steeply rising capacitance, suggestive of hydroxyl ion adsorption at potentials not too anodic to the p.z.c. The nature of the rapid increase in capacitance for NaOH will be discussed in greater detail in Chapter V in conjunction with the presentation of results for Na_2HPO_4 and Na_3PO_4 . A capacitance curve is shown in figure (19) for 0.1MNaOH ²⁶ which is essentially the same as observed for 0.1M KOH ⁸⁰.

Relatively little work has been published on the double layer characteristics of carboxylic acid salts. Capacitance studies by Grahame and Soderberg²⁹ revealed that specific adsorption of

acetate ions occurred only on a positively charged mercury electrode. Values of the charge due to anion specific adsorption were somewhat smaller in magnitude for acetate than for CO_3^{2-} , NO_3^- or SO_4^{2-} in 0.10 N solutions. Miller and Grahame³⁰ measured capacitance curves for mercury in 0.10M NaF, containing various amounts of sodium salts of dibasic and polybasic carboxylic acids. Of particular interest were their findings for the salts of oxalic, adipic, glutaric and 1,2,3 propanetricarboxylic acids. Like acetate, these anions were specifically adsorbed only on the positively charged electrode. There appeared to be a correlation between the amount of anion specific adsorption and the number of methylene groups in the different anions investigated. Specific adsorption was therefore attributed mostly to repulsive ion-water interactions caused by the hydrophobic methylene group.

Specific adsorption of phthalate ions was reported at coverages approaching a saturation limit on the uncharged mercury electrode³¹. Tilak and Devanathan³¹ proposed that the protonated carboxyl group underwent field-assisted dissociation in the large electrical field in the interphase. The aromatic ring of the phthalate ion, contributes to π -orbital interactions with the electrode^{110,111}. Adsorption studies in trisodium citrates solutions are in some ways comparable to the work on sodium p-toluenesulphonate described by Parry and Parsons³². This is particularly interesting because a peak is observed in the plot of specifically adsorbed anion charge versus electrode charge; a similar effect will be shown to occur in citrate salts. In the p-toluenesulphonate case the adsorption behavior was explained on the basis of two different orientations

of the ion at the electrode surface. At low coverages the anions could lie flat with the aromatic ring on the surface. At higher coverages repulsive interactions forced the anions to take up a less crowded configuration with the charged, hydrophilic group ($-\text{SO}_3^-$) pointed towards the bulk of solution. This type of two-point orientation behavior had been previously reported for the adsorption on mercury electrodes of heterocyclic bases and their conjugate ions^{110,111}.

Bockris, Devanathan and Muller¹⁰ proposed that the type and extent of ionic hydration are important to the specific adsorption process. As noted above, there is some merit to this concept for the alkali metal cations, and halide anions. The fact that hydrogen ions³³ and hydroxyl ions²⁶ show little specific adsorption at mercury electrodes is also consistent with the ability of these ions to be directly incorporated into the water structure. The strong specific adsorption of the highly polarizable iodide ion on the other hand, may be related to the difficulty with which it is able to accommodate itself in the water matrix¹³⁵. Many ions which do not readily fit into the tetrahedral cavity structure of water, due either to their size or shape, have been found to exhibit specific adsorption (eg. Cs^+ , Cl^- , Br^- , ClO_3^- , NO_3^- , ClO_4^- , IO_4^- , PF_6^- and tetraphenylborate). Other ions which either, because of their small size or ability to participate in hydrogen-bonding with water show very little tendency towards specific adsorption (eg. Li^+ , Na^+ , F^- , NH_4^+ , SO_4^{2-} , acetate and Mg^{++}). Tilak and Devanathan³¹, and Payne³⁵ reported that NO_3^- is specifically adsorbed with its hydration intact. This modelistic interpretation was used to

explain the low saturation coverages observed in NH_4NO_3 solutions. However, ion-pairing effects could be important in this case³⁶. De Levie and Kreuser³⁷, in a study of sodium trifluoromethanesulphonate suggested that the structure breaking properties of this ion and others (ClO_4^- and NO_3^-) in water were related to their specific adsorption. Barradas and Sedlak³⁸ were able to explain the limited adsorption of tetrahydrofurfuryl alcohol by considering the overlap of the hydration cospheres of the organic polar groups with those of the sulphate anion, used as a base electrolyte. The importance of ionic hydration has also been invoked frequently to explain the discrepancies between relative surface excesses calculated from diffuse layer theory and those obtained directly by experimental measurement. The case of NaH_2PO_4 was mentioned above²², in which the electrode was found to be covered by a layer of adsorbed water in the absence of ionic specific adsorption. Similar results were reported for sodium perchlorate solutions³⁹. Negative values of the charge due to specifically adsorbed Li^+ , Na^+ and Mg^{++} (ie. $q_+^i < 0$) were attributed to an ion-free layer on the electrode surface by Harrison et al.⁴⁰. Their results showed that the thickness of this layer increased with the degree of cation hydration, in agreement with adsorption phenomena at the electrolyte solution - air interface. Although it does not negate their final conclusions, these authors have used an erroneous term for adsorption of water in their GCS theory calculations (see reference 40, equation (5); cf. section D above). In fact, what they have calculated is the surface excess of water in the double layer (see equations (5) and (5a) in section D) by assuming that

the Gibbs dividing surface and the OHP are coincident. Schiffrin, in another paper⁴¹, also stated erroneously that Γ_w can be calculated from diffuse layer theory (see equation (4) in reference 41).

A comprehensive review on recent progress and problems in double layer studies has been published this year by Payne¹²⁹. He concludes that the nature of specific adsorption forces remains uncertain, but indicates there is little doubt that hydration, both at the interface and in the solution, makes an important contribution to the adsorption energy. The fact that polyatomic ions such as ClO_4^- , PF_6^- , NO_3^- and SCN^- are more strongly adsorbed from water than from dimethylformamide solutions is seen as confirmation of the prominent role of solvation in the adsorption process¹²⁹.

The interaction of solvent molecules with the electrode surface has frequently been related to the appearance of a hump in double layer capacitance curves^{10,132}. In both aqueous and non-aqueous solutions the hump usually occurs at small positive electrode charges ($6 < q_m < 0 \text{ } \mu\text{C cm}^{-2}$). This can clearly be observed for the capacitance curve shown in figure(2) for 0.1M aqueous trisodium citrate. Theoretical treatments^{130,112} invoking solvent reorientation in the inner layer, have been partially successful, but do not explain the lack of symmetry about the hump. Results of more recent investigations in non-aqueous solvents¹³³ indicate that solvent orientation phenomena are not wholly responsible for the hump. (In some instances two humps occur.)¹³³ Bockris and co-workers¹⁰ have considered the capacitance hump in water to be

due to specific adsorption of anions. This could cause the capacitance to go through a maximum since (dq/dE) must also reach a maximum value between zero coverage and saturation. However, there is plenty of evidence to support the view that the hump is due to a combination of solvent reorientation and ionic adsorption effects^{20,133,134}. Parsons²⁰ considers the isoelectronic series of ions: ClO_4^- , HSO_4^- and H_2PO_4^- as an example of this combined interaction. These ions are all about the same size, but differ in their effect on water. Perchlorate is a water structure-disordering ion, while HSO_4^- and H_2PO_4^- are both structure-ordering and heavily hydrated. Their adsorption at mercury reflects these different properties. At potentials negative to the p.z.c. the sequence of specific adsorption is $\text{ClO}_4^- > \text{HSO}_4^- > \text{H}_2\text{PO}_4^-$, but on positively charged mercury this is reversed. The magnitude of the capacitance hump is also in the order: $\text{ClO}_4^- > \text{HSO}_4^- > \text{H}_2\text{PO}_4^-$. It is likely that ClO_4^- facilitates the reorientation of adsorbed water dipoles in a changing electric field, but due to their stronger interactions with water the other two ions (HSO_4^- and H_2PO_4^-) reduce the orientational freedom of water dipoles.

There seems to be little doubt that adsorption of ions on electrodes is somehow related to the effect such ions have on the structure of water in the bulk phase. It is therefore important to consider a very useful, but semi-empirical supplementary source of structural information -- the viscosity of electrolyte solutions.

B. Viscosity and Structural Properties

The effect of a strong electrolyte upon the viscosity of the

solvent is given by the Jones-Dole equation⁴²:

$$\frac{\eta}{\eta_0} = 1 + AC^{1/2} + BC \quad (30)$$

where $\frac{\eta}{\eta_0}$ is the viscosity of the solution relative to that of the pure solvent, c is the molar concentration and A and B are temperature dependent constants and are characteristic of the electrolyte solution. The square-root term is attributed to ionic atmosphere effects⁴³ and the best determinations show close agreement between the experimental values of A and those calculated from a theoretical equation of Falkenhagen and Vernon⁴⁴. The A -coefficient represents the contribution from interionic electrostatic effects. The B -coefficient relates to ion-solvent interactions and is a measure of the order or disorder introduced by the ions into the solvent structure. It is often a characteristic and additive property of the individual ions of a strong electrolyte at a given temperature, but no theoretical basis has yet been established. Gurney⁴⁵ and others⁴⁶ have concluded that the B -coefficient for KCl should be equally divided between the two ions, and this assignment is generally accepted. At 25° the values are: $B_{K^+} = B_{Cl^-} = -0.007$. The ionic B -coefficients are proportional to the partial molal entropy of hydration⁴⁵. A positive ionic B -coefficient is a measure of the degree of order in the ionic co-sphere. The term co-sphere, refers to the spherical portion of solvent which encloses the ion and which is somewhat modified by the presence of the ion⁴⁵. Ions which possess negative coefficients act as structure disordering centres and cause the solvent to collapse about their surfaces. In general, structure making ions have positive ionic B -coefficients, and structure breakers have negative coefficients.

Nightingale and Benck⁴⁷ applied the theory of absolute reaction rates to show that the activation energy for viscous flow, $\Delta E^\ddagger$ is given by:

$$\begin{aligned}\Delta E^\ddagger &= R \frac{d \ln \eta_0}{d(1/T)} + \frac{R}{1 + Bc} \cdot \frac{d(1 + Bc)}{d(1/T)} \\ &= R \frac{d \ln \eta}{d(1/T)}\end{aligned}\quad (31)$$

The activation energy for viscous flow for the pure solvent is $\Delta E_0^\ddagger$. Assuming that the difference between $\Delta E^\ddagger$ and $\Delta E_0^\ddagger$ is equal to the sum of the activation energies of the ionic components one obtains:

$$\Delta E^\ddagger - \Delta E_0^\ddagger = v_+ \Delta E_+^\ddagger + v_- \Delta E_-^\ddagger \quad (32)$$

where $\Delta E_+^\ddagger$ and $\Delta E_-^\ddagger$ are the cationic and anionic activation energies, v_+ and v_- are the number of cations and anions, respectively, per molecule of salt.

Correlations exist with respect to the signs of the ionic B-coefficients and ionic activation energies, from which Nightingale⁴³ has proposed a classification. In class I the ions are small and due to the relatively large electrical fields at their surfaces one or more layers of solvent make up the ionic hydration co-spheres. These are structure makers and are characterized by positive ionic B-coefficients and ionic activation energies. They act to impede the viscous flow of solvent, but the effect decreases with increased temperature, presumably because the solvent "iceberg" around the ion is "melted" to a greater extent than is the "ice-like" structure of the bulk solvent. Class II ions are also structure makers, but they have negative activation energy. The electrical field at the ion surface is relatively weaker than class I ions, and therefore

orientation of water molecules are limited in extent. As temperature is increased solvent is apparently more susceptible to orientation about these ions. Class III consists of structure disordering ions whose ionic activation energies are also negative. Large ions which exhibit a peripheral (or hydrophobic) hydration are placed in class IV. They have quite large, positive ionic B-coefficients and positive ionic activation energies. They cause structure ordering of the solvent, because the hydrophobic ionic surface cannot participate in the "flickering clusters" of the solvent.

EXAMPLES OF NIGHTINGALE'S CLASSIFICATION

Class I Structure makers: Li^+ , Na^+ , Mg^{2+} , F^-

Class II Structure makers: Ba^{2+} , OH^- , SO_4^{2-} , $(\text{CH}_3)_4\text{N}^+$

Class III Structure breakers: K^+ , Cl^- , PF_6^- , NO_3^- , ClO_4^-

Class IV Structure makers: $(\text{n-C}_3\text{H}_7)_4\text{N}^+$, $(\text{n-C}_4\text{H}_9)_4\text{N}^+$

It is interesting that negative B-coefficients occur only in highly structured solvents like water, ethylene glycol, glycerol^{48,49}, deuterium oxide, and other associated solvents⁵⁰. The measurement of viscosity B-coefficients is a useful aid for investigating this aspect of liquid behavior, and it is used in this thesis to study the structural effects of aqueous citrate and phosphate solutions.

Certain other properties of electrolyte solutions are worthy of mention, especially with regards to carboxylic acid salts. Lindenbaum⁵¹ reported a relationship between the viscosity and apparent molal heat content for tetra-n-alkylammonium cations and large organic anions. Both the ionic B-coefficients and apparent

molal heat contents increase with the size of the tetra-n-alkyl ammonium cations. For large organic anions: acetate, butyrate and valerate the same trend is observed for the apparent molal heat content. It will be shown later that the ionic B-coefficients also follow a parallel scheme. The suggestion of importance here is that the large organic anions promote the structure of water, presumably by enhancing the degree of hydrogen bonding of the solvent. Gurney⁴⁵ has also pointed out the interesting consequences related to the localization of charge on the carboxylic group in the acetate ion. The neutral acetic acid molecule has a B value of 0.117 while the anion has $B = 0.25$. In the vapour phase an isolated acetate ion will resonate between the form $\text{CH}_3 - \text{C} \begin{smallmatrix} \nearrow 0 \\ \searrow \text{O}^- \end{smallmatrix}$ and the form $\text{CH}_3 - \text{C} \begin{smallmatrix} \searrow \text{O}^- \\ \nearrow 0 \end{smallmatrix}$. If this were also true in aqueous solution, the negative charge would appear to be spread out over a large volume. The ionic field would therefore be weak, but the fact that the viscosity B-coefficient of the acetate ion has a greater positive value than that of the acetic acid molecule, suggests that this is not so. The larger B-coefficient for the anion indicates that the negative charge is localized on one oxygen atom or the other and consequently enhances the ability of the ion to produce order in its hydration co-sphere.

It is a general observation that in not too concentrated aqueous solutions many carboxylic anions do not tend to dimerize⁵². This is a hydration phenomenon; the carboxylic group is water structure-ordering and can interact with one or more water molecules to promote hydrogen bonding in solution. The triply charged citrate anion offers the possibility of forming at least three or four

hydrogen bonds with water molecules through participation of its hydroxyl and three carboxylic groups.

One would anticipate that orthophosphate ions might likewise participate in the hydrogen-bonded network of water in a comparable way to citrate ions. Infrared spectra for aqueous trisodium citrate⁵³ indicate a shift of the O - H stretching frequency to lower energies. Similar effects are observed for acetic acid and disodium hydrogen phosphate^{43,53}, lending support to increased hydrogen bonding of water. The results of Hartmann¹²⁴ on the infrared O - H stretching vibrations in the presence of sodium carboxylates show a similar decrease in frequency which is due mainly to the presence of the carboxylic groups rather than the alkyl functions. The influence of some other oxy-anions (eg. SO_4^{2-} , HPO_4^{2-} and H_2PO_4^-) on the combination bending and stretching modes of water is also discussed by Nightingale⁴³.

According to Gurney⁴⁵, interaction between oppositely charged ions increases if both exert a similar kind of structural effect on the surrounding solvent. In figure (5) three successive states of ion-pair formation are shown schematically as described by Conway⁵⁸. The Gurney concept of water structure-enforced ion-pairing can be seen most clearly in figure 5(c) in which the waters of ionic hydration align themselves in an electrostatically favorable coordination with respect to the two ions of opposite charge. If both ions are water structure-ordering, this type of ion-solvent

Figure 5. States of ion-pair formation.
(from ref. 58)

- (a) ion contact type,
- (b) shared hydration shells, and
- (c) hydration shell contact type.

configuration is enhanced and is therefore known as water structure-enforced ion-pairing. On the basis of Gurney's proposed model, it is pertinent to investigate the viscosity B-coefficients for citrates and phosphates and to attempt an interpretation in terms of structure-ordering or structure-disordering effects in aqueous solutions. It is also interesting to compare the viscosity A-coefficients, because they relate directly to ion-ion electrostatic interaction and can be calculated theoretically⁴⁴. Thus, ion association properties may also be indirectly inferred from viscosity studies through the phenomenological Jones-Dole equation (cf. 44).

C. Ion Association in Solution and in the Double Layer

The association of citrate ions with alkali and alkaline earth metal cations is well documented⁵⁴⁻⁵⁶. Of particular interest to this work are the formation constants reported by Rechnitz and Zamochnick⁵⁴ for alkali metal cations in association with citrate ions at pH values where the predominant anionic species is the citrate³⁻ ion. The formation constant decreases in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ in accordance with behavior observed in other systems in which the anion is a structure maker³⁶. Prue³⁷ considers this to be connected with ionic hydration effects, and supports Gurney's concept of structure-enforced ion-pairing. The tendency towards association decreases in the reverse order (ie. Rb^+ to Li^+) when the counter ions are structure breakers³⁶.

Since ion association occurs in homogeneous electrolyte solutions, it is conceivable that these types of interaction may play a commensurately important role in the double layer. The adsorption of ions at an electrode is a specific heterogeneous situation

analogous to the association in homogeneous solutions between oppositely charged ions. This point is discussed most convincingly by Conway⁵⁸ and Conway and Gordon². In the electrode-solution interphase ion-pairs would come under the influence of two counter-acting forces. The extent to which these forces are effective depends on the electrode charge and the population of the various ionic species in the interphase. Contributions are made to the electrical field in the interphase by both the ions present and the state of charge of the electrode. In the first instance, orientation polarization of solvent molecules leads to a decrease in the dielectric coefficient. Several attempts have been made to predict the extent of dielectric saturation, from which it is reasonable to suggest that near the OHP the dielectric coefficient of water may be reduced to about $6-10^{10,59,112,113}$ from its normal value of 78.54 at 25°. Hasted, Ritson and Collie⁶⁰ have shown, even in the homogeneous phase of solution, that the macroscopic dielectric coefficient is reduced by 20-30% for electrolyte concentrations of about 2M. A small value for the dielectric coefficient in the double layer will be reflected by an increase of electrostatic forces between oppositely charged ions relative to the weaker coulombic forces due to ions in the bulk solution of higher dielectric coefficient. Thus an enhancement of ion-pairing is envisaged for the double layer, based solely on a dielectric saturation effect.

A second force, which should oppose electrostatic attraction between ions, is the large electrical field present in the inter-^{120,138}phase. Such fields are comparable to those existing at the surface

of a small spherical ion and may be in the range: 10^6 to 10^8 volts cm^{-1} . Field dissociation effects are assumed to be operative under such conditions and have been considered by some workers, especially for homogeneous chemical reactions of weak protic acids in the double layer⁶¹. The field-dissociation, or second Wien effect^{81b,136}, has been given a quantitative and theoretical explanation by Onsager and Wilson^{81b}. According to this theory the high-field enhancement of conductance arises due to destruction of the ionic atmosphere (first Wien effect), which in turn increases the degree of dissociation of any ions combined in pairs. The probabilities of ion collisions leading to association compared to the probability of dissociation against or with the field direction are modified with respect to the situation at zero field. The nature of ion association and structure in concentrated solutions and molten salts is closely connected with the problem of the e.d.l. in which ionic concentrations are extremely large. A "quasi-dipolar solid lattice" model, based on Fröhlich's theory¹³⁷, was proposed by Barradas and Sedlak⁵⁹ to treat this aspect of the double layer. Some of the results of this dissertation will be found to concur with this line of reasoning. In view of ion-pair formation reported for trisodium citrate solutions, the double layer results were interpreted by considering the possible influences of dielectric saturation and field-dissociation on ion-pairs in the high-field region near the electrode.

In a relatively recent paper by Jenard and Hurwitz⁶², the effect of strong electrical fields on ion-pairing in the double layer is accounted for in a comprehensive theoretical approach combining both dielectric saturation and field-dissociation. What follows is

a review of the salient concepts and developments introduced by Jenard and Hurwitz in their mathematical treatment of this complex problem.

Consider an ion-pairing reaction at equilibrium in the solvent, water:

where z_n is the ionic charge of species A_n ($n = 1, 2, 3$), and $\phi(x)$ is the electrostatic potential at position x . The macroscopic electric field, $F(x)$ and polarization, $P(x)$ are directed along the x -axis.

At some arbitrary distance from x ($x = x_b$), $\phi(x_b)$, $\bar{F}(x_b)$ and $P(x_b)$ are assumed to vanish. At equilibrium it is further assumed that:

$$P(x) = P_0(x) + P_i(x) \quad (34)$$

The term $P_0(x)$ is taken to include the solvent and ionic species A_1 and A_2 , which are referred to collectively as the "medium". The polarization, $P_i(x)$ corresponds to the average "internal dipole moment" per unit volume of the ion-pairs, A_3 in the field $F(x)$ ^{62,118}. In the case of the "medium", the field, polarization and dielectric coefficient are related as follows:

$$\frac{P_0(x)}{\bar{F}(x)} = \frac{\epsilon_0(x) - 1}{4\pi} \quad (35)$$

An equation given by Booth⁶³ is now introduced for the dependence of $\epsilon_0(x)$ on high electrical field strength.

$$\epsilon_0(x) - \epsilon_0^\infty = (\epsilon_0^0 - \epsilon_0^\infty) \left(\frac{3}{y}\right) L(y) \quad (36)$$

Equation (36) uses the Langevin function: $L(y) = \coth(y) - y^{-1}$,

where $y = b^{\frac{1}{2}} \bar{F}(x)$. The static dielectric coefficient of water, in the absence of a field¹¹⁹ is $\epsilon_0^0 = 78.54$ (at 25°), and ϵ_0^∞ is the limiting value for ϵ_0^0 when orientation polarization is saturated. In accordance with findings by Glueckauf⁶⁴, $\epsilon_0^\infty = 5.5$. Previously, the visible light wavelength value for the refractive index of water, n_r had been employed: $\epsilon_0^\infty = n_r^2 = 1.76$, but Glueckauf has shown that better agreement is obtained for observed and calculated hydration entropies using $\epsilon_0^\infty = 5.5$. Such a value corresponds to the long wavelength determination for n_r . The dielectric coefficient calculated using equation (36) is an average value over the whole water molecule, and as pointed out by Booth⁶³, a limitation of his dielectric model is that it is valid only for $\epsilon_0(x) \gg \epsilon_0^\infty$ and for a homogeneous field. Any use of the Booth equation must be somewhat limited, but so far, it is the best theoretical equation available⁶⁴.

In equation (36), for pure water $b = 5.65 \times 10^{-8}$ when $\bar{F}(x)$ is expressed in electrostatic units^{63,64}. The ionic strength dependence of b is assumed to be given by:

$$b = h(\epsilon_0^0(x) - \epsilon_0^\infty)^1 \quad (37)$$

where $\epsilon_0^0(x)$ is the dielectric coefficient of the "medium" when $\bar{F}(x) = 0$, 1 is an adjustable parameter: ($1 < 1 < 2$), and h can be evaluated from results for pure water thus:

$$h = \frac{5.65 \times 10^{-8}}{(78.54 - 5.5)^1} = 5.65 \times 10^{-8} (73)^1 \quad (\text{e.s.u.})^{-2}$$

Equation (37) in conjunction with (36) was found to give results for $\epsilon_0(x)$ in good qualitative agreement with Booth's theory for

small fields and dilute electrolyte solutions⁽⁶²⁾. Additionally, the use of equation (37) is consistent with both experimental results⁽⁶⁰⁾ and theoretical predictions⁽⁶³⁾ for strong fields where the onset of dielectric saturation occurs with increasing $\bar{F}(x)$ and increasing ionic strength. The work of Hasted, Ritson and Collie⁽⁶⁰⁾ is taken as grounds for a further assumption, that for ionic concentrations, C_n up to about 2M, $\epsilon_o^0(x)$ is linearly dependent on C_n :

$$\epsilon_o^0(x) = \epsilon_o^0 + \sum_n C_n \delta_n \quad (38)$$

In equation (38) δ_n is the dielectric decrement for ionic species A_n , and is given by:

$$\delta_n = \left(\frac{\partial \epsilon_o^0(x)}{\partial C_n} \right)_{T,p,\sum_{n' \neq n} C_{n'}} \quad (39)$$

Hasted and co-workers⁶⁰ have separated the dielectric coefficient of NaCl into its ionic components, δ_+ and δ_- on the basis of ionic hydration theory. Comparison of several electrolytes gave values of the ionic dielectric decrements (δ_n) and these are listed below, as taken from the paper by Hasted et al. (loc. cit.).

	H^+	Li^+	Na^+	K^+	Rb^+	Mg^{++}	Ba^{++}	La^{+++}	F^-	Cl^-	I^-	OH^-	SO_4^{--}
δ_n :	-17	-11	-8	-8	-7	-24	-22	-35	-5	-3	-7	-13	-7

The δ_n are negative quantities which provide for a more or less important decrease in $\epsilon_o^0(x)$, depending on the interaction of ions with water molecules. Ionic species in aqueous solutions have negative δ_n whether they increase the order of solvent dipoles in their own electrical fields, or act as solvent structure disordering

centres, or produce a cavity of small dipole moment^{62,120}.

The next step in the Jenard and Hurwitz derivation is to formulate an expression for the free energy density change accompanying a variation in the polarization. In a closed equilibrium system, subject to an electric field, the change in the free energy density, df , is given as^{118,120}:

$$df = \frac{dG}{V} = \frac{1}{V} \left(\sum \mu_i dN_i - SdT + Vdp \right) + \bar{F}dP \quad (40)$$

where the various symbols have their usual thermodynamic meaning¹¹⁸: V (the total volume), G (Gibbs free energy), μ (chemical potential), N (mole number), S (entropy), T (absolute temperature) and p (hydrostatic pressure). From equation (40), the field at constant T , p and c_i is given by:

$$\bar{F}(x) = \left(\frac{\partial f(x)}{\partial P(x)} \right)_{T,p,c_i} \quad (41)$$

Integration of (41) gives the free energy density in the presence of a field:

$$f(x) = f_0(x) + \int_0^{P_0(x)} \bar{F}(x) dP(x) \quad (42)$$

where $f_0(x)$ is the free energy density when $\bar{F}(x) = 0$. The ion-pair equilibrium (equation (33)) may now be treated by first obtaining the free energy density leading to $P_i(x)$, keeping $P_0(x) = 0$, and afterwards charging the "medium" to its final value $P_0(x)$ ^{62,120}.

In this process the chemical potential would be:

$$\left(\frac{\partial f(x)}{\partial C_n(x)} \right)_{T,P,\sum_{n',s \neq n} C_{n'}} = \mu_n^0(T, P_i(x), \sum C_n(x)) + RT \ln a_n(P_i(x)) + \left[\frac{\partial}{\partial C_n(x)} \left(\int_0^{P_0(x)} \bar{F}(x) dP(x) \right)_{T,P,\sum_{n',s \neq n} C_{n'}} \right] \quad (43)$$

Equation (43) is valid for $n = 1, 2, 3$ and s , where s denotes solvent. The quantities, μ_n^0 and a_n , correspond to the standard chemical potential and to the activity of species A_n respectively; both being defined in a system in which A_3 takes its inner equilibrium configuration in $F(x)$, even though the solvent remains virtually unaffected by the field⁶².

When equation (35) is substituted into (43) it can be shown that:

$$\begin{aligned} \mu_n(T, P(x), \Sigma C_{n'}(x)) &= \mu_n^0(T, P_i(x), \Sigma C_n(x)) + \\ &RT \ln a_n(P_i(x)) - \frac{1}{8\pi} \int_0^{\bar{F}^2} \left(\frac{\partial \epsilon_0(x)}{\partial C_n(x)} \right) d\bar{F}^2_{T, \bar{F}, \Sigma C_{n'}, n', s \neq n} \\ (n = 1, 2, 3, s) \end{aligned} \quad (44)$$

The integrand in (44) can be rewritten in terms of v_n and v_s , the partial molar volumes of A_n and solvent, respectively¹²⁰.

$$\left(\frac{\partial \epsilon_0(x)}{\partial C_n(x)} \right)_{T, \bar{F}, \Sigma C_{n'}, n', s \neq n} = \delta_n + \frac{v_n}{v_s} \left(\frac{\partial \epsilon_0(x)}{\partial C} \right)_{T, \bar{F}, \Sigma C_{n'}, n'} \quad (45)$$

where C is the molar concentration of the solute. For diffusion equilibrium¹²⁰ of A_1, A_2, A_3 :

$$\left(\frac{v_n}{v_s} \right) \mu_s(\bar{F}) + \mu_n(\bar{F} = 0) = \left(\frac{v_n}{v_s} \right) \mu_s(\bar{F} = 0) + \mu_n(\bar{F}) + Z_n F \phi(x) \quad (46)$$

The dissociation equilibrium constant for the reaction (equation (33)) is obtained in terms of the activities of the A_n ,

by combining equations (33), (36), (37), (38), (39), (44), (45) and (46):

$$K_d(\bar{F}) = \frac{a_1(\bar{F}) a_2(\bar{F})}{a_3(\bar{F})} = K_d(\bar{F} = 0) F_3(\bar{F}(x)) \cdot \exp \left[\frac{3\delta}{8\pi RT} \left(1y L(y) - 2(1 - 1) \log \left\{ \frac{\sinh(y)}{y} \right\} \right) \right] \quad (47)$$

In equation (47) $\delta = \delta_1 + \delta_2 - \delta_3$ and $F_3(\bar{F}(x)) = \exp \left[\frac{\mu_3^0(\bar{F}) - \mu_3^0(\bar{F} = 0)}{RT} \right]$

The equilibrium dissociation constants in the presence of a field and in the absence of a field are $K_d(\bar{F})$ and $K_d(\bar{F} = 0)$, respectively.

Jenard and Hurwitz now assume that $F_3(\bar{F}(x))$ takes the form of Onsager's equation for field-dissociation^{81b}.

$$F_3(\bar{F}(x)) = \frac{J_1(4[-\beta q]^{1/2})}{(2[-\beta q]^{1/2})} \quad (48)$$

In equation (48) J_1 is the Bessel function of order one, q is the Bjerrum distance and β is given by equation (49):

$$2\beta q = \frac{z_+^2 z_-^2 (\Lambda_+ + \Lambda_-)}{(z_- \Lambda_+ + z_+ \Lambda_-)} \cdot 9.636 \frac{\bar{F}(x)}{\epsilon_0 T^2} \quad (49)$$

in which $\bar{F}(x)$ is in units of volts cm^{-1} ; Λ_+ and Λ_- are the equivalent conductance for cations and anions, respectively. Onsager's equation relies on pure electrostatic-enforced ion-pairing in the absence of ionic atmosphere effects. It does not consider dielectric saturation in its derivation nor does the theory provide for ionic solvation in the external field, which leads to an increase in free energy as indicated in equation (44) if $\delta_n \ll 0$.

Inspection of equation (47) reveals that for very negative δ the field dissociation effect could be replaced by a predominantly

associative process. The values of $\log K_d(\bar{F})/K_d(\bar{F} = 0)$ have been plotted against the field $\bar{F}$ for the case of a uni-univalent electrolyte as calculated by Jenard and Hurwitz and are shown in figure (6). These results are for 25°C and $|z_1| = |z_2| = 1$. For the concentration dependence of y in equation (47) and $\epsilon_0^0(x)$ in equation (49) it has been assumed⁶², that on the average from use of equation (38), $\sum \delta_n C_n(x) \approx 15 \times 10^{-3} \delta$. Figure (6) indicates that the Onsager-Wien effect subsists for fields less than about 2×10^6 volt cm^{-1} , but at higher fields and very negative values of δ the trend towards association may prevail, depending on the degree to which the ions interact with water.

In the particular case in which $1 \rightarrow 2$ a minimum occurs in figure (6) (eg. curve C_2), indicating the attainment of complete dielectric saturation in the field, so that any further increase in field strength results only in a dissociative effect. However, for electrolyte solutions less than about 2M the dielectric coefficient is approximately proportional to concentration⁶⁰, therefore it is plausible to assume that l has a value not too different from unity. As shown in figure (6), the predictions of the Jenard and Hurwitz calculation are that in the vicinity of the OHP, where fields may be as large as 10^7 volt cm^{-1} , association would occur, depending on the abilities of the particular ions to interact with the solvent (curves a_1, b_1, c_1). This conclusion has profound implications, because it is the first theoretical treatment to suggest that association occurs in the double layer. Hitherto it has been widely accepted that dissociative effects play a role in the kinetics of certain double layer reactions^{61,66},

Figure 6. Variation of the ion-pair dissociation constant with electrical field according to ref. 62. $|z_1| = |z_2| = 1$, $T = 25^\circ\text{C}$ and $\langle \epsilon_o^\circ(x) - \epsilon_o^\infty \rangle = 73 + 1.5 \delta$

$\delta \text{ (mol}^{-1} \text{ l)}$	1	2
-10	a_1	a_2
-15	b_1	b_2
-20	c_1	c_2

but only a few studies have considered ion-association to be important^{103,104}. Gierst¹⁰³ and co-workers, in a very thorough paper on this subject, showed a correlation between bulk ion-pairing and the effects on electrode kinetics which could only be explained by invoking an ion-pairing reaction in the double layer. They concluded that increased rate constants for reduction of anions were intimately related to the extent of ion association. Electrostatic ion-pairing was found to be most frequently the important factor, but occurrence of "cavity-pairing" was also indicated. The direction and magnitude of these kinetic effects were accounted for on the basis of the Gurney concept⁴⁵ which stresses the importance of ion-water interactions. Accordingly, association can be expected to prevail mostly between oppositely charged ions of the same type. Gierst and co-workers proposed the following list of ions, which were positioned according to their charge and extent of their water-ordering character.

Ionic Behavior in Water (ref. 103)

Increasing	Field Strength Water Structure Ordering	Decreasing
<hr/>		
$\text{La}^{+++}, \text{Mg}^{++}, \text{Ca}^{++}, \text{Ba}^{++}$		
	$\text{Li}^+, \text{Na}^+, \text{K}^+, \text{Cs}^+, \text{Me}_4\text{N}^+, \text{Et}_4\text{N}^+, \text{etc.}$	
	$\text{F}^-, \text{OH}^-, \text{IO}_3^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{ClO}_4^-, \text{MnO}_4^-, \text{ReO}_4^-, \text{etc.}$	
$\text{Fe}(\text{CN})_6^{=}, \text{CO}_3^{=}, \text{SO}_4^{=}$		
<hr/>		
"Mostly electrostatic" ion-pairing		"cavity sharing"
<hr/>		

Association or pairing between water-ordering ions is typified by MgSO_4 or LiOH . In contrast, species like Et_4NI are examples of an inverse type of ionic interaction, in which pairing takes place by "cavity sharing", or in other words, "cavity pairing"¹⁰³.

In the derivation of equation (47) Jenard and Hurwitz have indicated⁶² some possible modifications to improve their theory. The value attributed to ϵ_0^0 in the Onsager-Wien expression (equations (48) and (49)) is uncertain, since Onsager obtained his equation by assuming a dielectric coefficient independent of the field.⁶⁵ In the calculations, Jenard and Hurwitz pointed out that the replacement of ϵ_0^0 by $\epsilon_0^0/8$ in equations (48) and (49) was equivalent to substituting a uni-univalent electrolyte by a divalent one. Another important consideration is the role of activity coefficients in the double layer and under high field conditions. Such factors are not precisely known for ions in the e.d.l., and are even less understood in the presence of strong electrical fields¹²⁰. However, if the ionic atmosphere is broken up in an intense electrical field, then the activity coefficient may approach unity. This is indicated by the first Wien effect in which the equivalent ionic conductance in large fields is observed to approach that at infinite dilution. If such is the case, the use of ionic concentrations for activities is not as bad as might otherwise be expected. However, Jenard and Hurwitz suggest that cavity field calculations are in order for such conditions¹²². One final criticism is the use of the Booth theory, which is limited if water molecules undergo field-dissociation.

The use of the Jenard-Hurwitz theory for unsymmetrical

electrolytes must take into consideration an appropriately revised form of the Onsager-Wien equation. For a binary electrolyte Jenard and Hurwitz showed that $F_3(\bar{F}(x))$ is a hyperbolic Bessel function, which is essentially that shown in figure (6) for $\delta = 0$. This results because the term βq in equation (48) is positive for a symmetrical electrolyte, due to cancellation of the z and Λ symbols in equation (49). For a 1:3 electrolyte βq will be negative and therefore $F_3(\bar{F}(x))$ will have a real numerator and real denominator, resulting in a normal first order Bessel function. This function is oscillatory and decreases in amplitude for increasing argument (ie. field). Hence, the shape of the $\log K_a(\bar{F})/K_a(\bar{F} = 0)$ vs. $\bar{F}$ plot will be different for a 1:3 electrolyte than for the binary case shown in figure (6). However, the general conclusions made by Jenard and Hurwitz will be essentially unchanged for negative values of δ and this is the factor of prime importance to the present work.

In summary it is important to reiterate the conditions for which ion-association is predicted for the double layer by Jenard and Hurwitz. These are: (a) a high electrical field in the region of the OHP, 10^6 to 10^7 volt cm^{-1} , (b) strong interaction between ions and water molecules and (c) a co-operative ion-solvent interaction stressing water structure-enforced ion-pairing. Although this theory has certain limitations and may be subject to improvements it is an important one in originality and recognition of effects in the double layer previously not considered by models proposed by other workers.

CHAPTER IIIEXPERIMENTALA. Methods of Studying Adsorption at Charged Interfaces

Ionic adsorption at the mercury-electrolyte interface was studied by two complementary experimental techniques. The double layer capacitance was measured by a phase-sensitive a.c. method which produced a continuous and automatic recording of capacitance as a function of applied potential. Interfacial tension data were obtained by the direct method using a Lippmann capillary electrometer of modern design, the details of which were described previously¹⁰⁹. The streaming mercury electrode technique (similar to Grahame's type V method⁷³) provided accurate results for potentials of zero charge. Viscometric and other ancillary measurements were made in homogeneous electrolyte solutions to aid the analysis of double layer data. These additional diagnostic quantities were used to complement the double layer data and to correlate the homogeneous and heterogeneous electrochemical results. In this chapter the double layer and auxiliary experimental methods will be described.

Electrocapillary and capacitance curves were acquired for between seven and ten solution concentrations, generally in the range: $5 \times 10^{-3} \text{M}$ to 1.0M , depending on electrolyte solubility. Detailed double layer studies were made of the following aqueous electrolytes at a mercury electrode at 25°C :

- (a) disodium hydrogen orthophosphate (Na_2HPO_4)
- (b) trisodium orthophosphate (Na_3PO_4)
- (c) disodium hydrogen citrate (Na_2HCit)
- (d) trisodium citrate (Na_3Cit)

Although several other electrolytes were examined, the results were not sufficiently reliable to warrant presentation or to augment the central theme of the thesis. These later results (eg. of MgSO_4) are only of limited interest to the main thrust of this research project. Unless otherwise stated they will not be discussed unless there is a rationale for making appropriate inferences, deductions and comparisons to them.

B. Electrocapillary Measurements

Interfacial tension (γ) data were measured as a function of electrode potential (E) using a modern Lippmann capillary electrometer¹⁰⁹. The electrode system consisted of a platinum wire counter-electrode, a reference electrode (SCE) and the capillary which was connected to a reservoir of mercury. The level of the mercury column was approximately 0.1 cm above the tip of the capillary and could be observed with reference to a fiducial mark which had been scratched onto the outer surface of the finely tapered capillary tip. The mercury was polarized by applying a potential difference between it and the counter-electrode, using a lead sulphate storage battery. The potential of the mercury electrode (E) was then measured against reference electrode employing the potentiometric mode of a pH meter (Radiometer pH meter-4). Figure (7) is a schematic diagram of the complete Lippmann apparatus, showing the electrical connections between the electrode system and polarizing circuit.

After the applied voltage was set to the desired value, the mercury was forced, by nitrogen gas pressure, to the fiducial mark on the capillary electrode and the manometer pressure reading was

Figure 7. Schematic diagram of capillary electrometer.

observed with a precision cathetometer. Two or three drops of mercury were expelled from the capillary after each reading so as to expose a fresh surface for the next observation. Data were obtained, at first near the e.c.m., followed by altering the potential settings to either side of the e.c.m. until a complete curve had been covered. Finally, four to six additional observations were taken near the e.c.m. If these latter data points agreed to within 0.003 cm (manometer height reading) with the initial points this was taken as satisfactory repeatability (see also Chapter IV).

The bore of the capillary at the reference mark was calibrated using 1.0M KCl whose e.c.m. is: $\gamma^{\max} = 424.2 \text{ mNm}^{-1}$ and $E_z = -0.515$ volts against the SCE. The traditional units for interfacial tension (dyne cm^{-1}) have been replaced by S.I. units (milli Newtons per meter) and these will be used throughout the thesis. Frequent capillary calibrations were done during the course of the experimental work to detect any changes in the effective radius of the capillary electrode.

The following formula¹³⁵ was employed in calculating γ as a function of E:

$$\gamma = \frac{rg}{2} \left\{ d_{\text{Hg}} (2 [h - h_o] + h_c) - d_s h_s \right\} \quad (50)$$

The capillary constant is $rg/2$, where g is the gravitational constant and r is the radius at the reference mark. Other symbols in equation (50) are:

- d_{Hg} : density of mercury
- d_s : density of solution
- h : height of mercury in one limb of the manometer when capillary reservoir pressurized

- h_o : height of mercury in manometer for unpressurized capillary reservoir (ie. normal ambient pressure)
- h_c : height of mercury in reservoir above capillary reference mark
- h_s : height of solution surface above capillary reference mark.

The electrochemical cell and other apparatus will be described in section E.

C. Differential Capacitance Measurements

1. Basic Principles

The most versatile and accurate method of directly measuring the differential capacitance of the e.d.l. is by means of alternating current techniques (a.c.). A small a.c. signal of known frequency is superimposed on the polarizing d.c. potential, applied between the working and counter electrodes. The total cell impedance is then measured with an impedance bridge using null detection. The impedance of the counter electrode is kept very small by ensuring that its surface area is much larger than that of the working electrode. Since the electrodes are in series, the capacitance of the working electrode is essentially equal to the measured cell capacitance due to the large surface area differences.

The most accurate capacitance results are obtained using impedance bridges of sophisticated design⁶⁷ based on a prototype first reported by Grahame and Parsons¹⁰⁸. The dropping mercury electrode is preferred by most workers, because it minimizes contamination of the electrode due to the presence in solution of

adsorbable impurities. The experimental apparatus is rather elaborate and the procedure is very time-consuming and tedious. In the present work a slightly less accurate, but faster technique was employed and permitted the automatic recording of a capacitance curve in a matter of twenty minutes. The basic operating principles, calibration and procedures will be given in the following subsections.

2. Capacitance Recording Apparatus

A block diagram of the capacitance recording instrumentation is shown in figure (8). The polarograph (Radiometer, model PO-4) serves two functions: (1) it supplies the d.c. potential ramp (100, 200, 400 or 800 mV min⁻¹) across the terminals of the electrochemical cell, and (2) simultaneously records the output signal derived from the Kowalski-Srzednicki^{68,69} circuit. The main electronic circuitry is given the name of those who first published the description of its operation. Superimposed on the d.c. potential is an a.c. voltage of frequency, ω and r.m.s. amplitude, $\bar{V}$ which is obtained from a sine wave generator (Hewlett Packard, model 202A). A d.c. power supply (Harrison Laboratories, model 6224A) provides 14 volts to the Kowalski-Srzednicki circuit.

The details of operation and uses of the Kowalski-Srzednicki circuit have been published⁶⁸⁻⁷¹. The device employs negative feedback for stable amplification and uses a phase detector to produce a full wave rectified output. This is fed to the polarograph and after further amplification is recorded as a current which is proportional to:

$$\frac{\omega C' |\bar{V}|}{1 + (\omega RC')^2}$$

Figure 8. Schematic diagram of the automatic capacitance recording apparatus.

In practice ω , $\bar{V}$ and the resistance of the electrochemical cell, R , are fixed quantities. When $\omega RC' \ll 1$, the recorder deflection is then proportional to the total capacitance of the cell, C' . The value of R may be kept sufficiently small by using a low impedance reference electrode and locating the working electrode at not too great a distance from it.

3. Calibration

The recorder scale of the polarograph is calibrated by replacing the electrochemical cell in figure (8) by an analogue circuit consisting of a decade resistor and decade capacitor in series. The generator frequency, ω is set to the required value and the amplitude of the applied a.c. signal is adjusted by the generator output control and a variable resistor in the voltage divider of the Kowalski-Srzednicki circuit. An a.c. voltage of 10 mV (peak to peak) was selected in all cases. Using a commercial impedance bridge (General Radio, type 1608A), R is measured for a known area of the working electrode (cathode C in figure (8)). In all studies this was a hanging mercury drop electrode (see section E.2). The recorder scale is selected to accept the desired range of capacitor values (usually 0.50 to 1.80 μF) and the zero or bias level is then adjusted by controlling the output of the Kowalski-Srzednicki circuit. The analogue circuit resistor is set to R and the decade capacitor is varied in steps from minimum to maximum values to produce corresponding deflections of the recorder pen. The calibration curve is then plotted using recorder deflection and analogue circuit capacitance as the coordinates.

With this procedure it was possible to operate into the non-linear response region up to $\omega RC' < 0.5$. Unless otherwise stated, the following instrument settings were used for recording capacitance curves:

- 1 : $\omega = 35 \text{ Hz}$
- 2 : a.c. voltage 10 mV peak to peak
- 3 : maximum value of dummy cell capacitor = $2.11 \mu\text{F}$.

For these conditions the maximum practical value of cell resistance was about 7 Kohm. This limited recording of capacitance curves to solutions more concentrated than approximately 10^{-3}M , depending on the electrolyte, distance between working and reference electrodes and the area of the mercury surface.

4. Procedure

The procedure followed in obtaining a capacitance curve will be described for a typical experiment. After calibration a switch is thrown to connect the electrochemical cell to the recording circuit. Appropriate dials are selected on the polarograph to determine the starting potential ($E = -1.60 \text{ volts}$), voltage sweep rate (400 mV min^{-1}) and sweep direction (towards positive potentials). The bracketed items just given, were for a typical run and could be altered to suit the individual experiment. A mercury drop of known surface area (eg. 0.041 cm^2) is hung on the working electrode (see section E.2) and the recording is started by switching on the drive mechanism of the polarograph. When the potential reaches its positive limit, the sweep direction is reversed and finally stopped when the original starting potential has been

achieved. In this way one actually obtains a recording of two superimposed capacitance curves for a single drop of mercury. The same procedure can be repeated with the starting potential selected to the most positive value. Repetitive runs are obtained to ensure reproducibility and to observe whether the capacitance curves are affected by the rate at which the potential is swept or the value selected for the starting potential. If the solutions contain adsorbable impurities anomalous curves are readily distinguished by the appearance of small peaks which usually cannot be reproduced from run to run. The attainment of reproducible capacitance data was accepted as an indication of results corresponding to equilibrium capacitance measurements.

Data points were taken from the recorder chart paper at 25 and 50 mV intervals positive and negative of the e.c.m., respectively. The differential capacitance per unit area was calculated from the calibration curve and known mercury drop area.

D. Auxiliary Measurements

1. Streaming Potentials

The flatness of the electrocapillary curve near the apex makes it difficult to obtain accurate values for the potential at which zero charge occurs. In addition, the anodic branch of the electrocapillary curve may be lower than the corresponding results obtained by double integration of capacitance curves. This frequently occurs in solutions more dilute than about $0.01M^{72}$. The effect of this is to shift the e.c.m. potential in the negative direction. Such problems have been observed in numerous cases in which the Lippmann

capillary electrometer was used. An alternate method of determining the potential of zero charge (p.z.c.) is the streaming mercury electrode technique⁷³. In following discussions e.c.m. will be used when referring to the potential of the electrocapillary maximum and p.z.c. will be reserved for streaming potentials.

A fine stream of mercury droplets is allowed to flow from the tip of a tapered capillary tube which is submerged in the test solution. After some time the potential of the mercury stabilizes and this measurement is taken as the p.z.c. The apparatus used in this work is quite simple. A suitable capillary produced an "umbrella-like" shower of mercury when the reservoir was subjected to a pressure of about 5 psi above normal atmospheric pressure. Electrical connection was made by a 1 cm length of platinum wire sealed into the glass tubing between the capillary and the mercury reservoir. Immediately above this a teflon stopcock was located so that the mercury flow could be halted when the electrode was not in use. The streaming electrode was connected by a ring-seal joint to a tank of compressed nitrogen gas via a Hoke type control valve. This allowed for the application of an external pressure in addition to the mercury head which was approximately 25 cm.

The tip of the streaming electrode was immersed about 5 cm in the electrolyte and a sensitive voltmeter (Keithley Potentiostatic Electrometer, model 603A) was connected between it and a SCE. Mercury was permitted to flow for about 15 min. before the potential difference was measured. Solutions were stirred and de-aerated by bubbling purified nitrogen gas (see section E.3). The potential of the streaming electrode was recorded as a function of externally

applied pressure in quiescent solutions (ie. N_2 bubbling interrupted). Measured potentials generally attained a steady maximum value for pressures between 10 and 20 psi and these were accepted as the p.z.c. values. In most cases the p.z.c. was observed to fluctuate by as little as ± 0.02 mV (cf 114).

2. Sodium Ion Electrode Potential

The potential differences between a SCE and a sodium ion responsive electrode (Fisher No. 1363920) were measured with a Keithley potentiostatic electrometer (model 630A). Solutions were thermostated to $25.0 \pm 0.1^\circ\text{C}$ and the Na^+ electrode shielding was connected to the low input of the measuring instrument. For phosphate solutions (Na_2HPO_4 and Na_3PO_4) the electrode was calibrated against standard NaOH solutions (10^{-1} , 10^{-2} , 10^{-3} and 10^{-4} M). In other work NaCl standards were employed (10^{-1} , 10^{-2} , 10^{-3} , 5×10^{-1} , 1.0 and 2.0 M).

Calibration was required for three reasons:

- (1) to ensure proper response of the sodium ion electrode,
- (2) to enable detection of changes in Na^+ activity in sodium citrate solutions,
- (3) to evaluate the actual shape of plots of $\ln a_{\pm}$ versus electrode potential for different electrolytes. Such information was required for thermodynamic analysis of double layer data.

3. Viscosity and Density Measurements

Data for viscosity calculations in electrolyte solutions were

measured using a Cannon-Fenske viscometer (Cannon Instrument Co., size 50). The viscometer was clamped to a metal rod which was aligned to within about one degree arc of the vertical. This assembly was mounted in a water bath whose temperature was controlled to a tolerance of $\pm 0.05^{\circ}$. Efflux times were obtained with a stopwatch (Jaquet serial No. 635513) which could be read to about ± 0.05 sec. For each solution investigated ten efflux times were measured and the average reading calculated. Mean deviations were about 0.1 sec, which is approximately the reflex time of the stopwatch operator. An aliquot of test solution of 5.00 ± 0.01 ml was delivered by pipette into the clean, dry viscometer and two or three preliminary runs were made before recording efflux times. This allowed about ten minutes for thermal equilibrium to be established between the test solution and the viscometer apparatus.

A set of experiments consisted of measuring efflux times for all concentrations in the set; these were usually: 0.005, 0.010, 0.020, 0.030, 0.040, 0.050, 0.0625 and 0.100M. In some systems data were obtained for concentrations up to 1.5M. Before a set of experiments the viscometer was carefully cleaned with hot concentrated nitric acid followed by prolonged rinsing with distilled water. The final rinse water (triply distilled) was checked for conductance to ascertain removal of all acid. Drying was done in an oven at 100° for a period of at least five hours. Triply distilled water was used to calibrate the viscometer before and after a set of experiments. Typical efflux times for two such calibration runs were observed to change by only 0.20 sec. in a total time of 220 sec.

Relative viscosity was calculated by:

$$\frac{\eta}{\eta_0} = \frac{td}{t_0 d_0} \quad (51)$$

where η/η_0 is the viscosity of the solution relative to water at the same temperature. The zero subscript refers to water; t is the efflux time and d the density. For pure water the density at 25° (relative to that at 4°), was taken as 0.99708 g/ml⁷⁴.

A pycnometer, 25 ml nominal volume, was used for density measurements at 25°. Calibration was done before and after a set of electrolyte density measurements, using triply distilled equilibrium water. Density data were accurate to about $\pm 5 \times 10^{-5}$ g ml⁻¹. Electrolyte densities were required for relative viscosity calculations as indicated in equation (51).

4. Measurement of pH

All pH readings were made using a Radiometer pH meter-4, equipped with a SCE and glass electrode (Radiometer Type G200B). Measurements were taken at room temperature: 22°-23°. The instrument was calibrated with standard buffer solutions: pH = 7.00 or pH = 10.00, whichever was closest in pH to the solution being examined. Maximum reading error was ± 0.02 pH units.

5. Voltammetry

Current versus potential curves were obtained in all systems for which double layer data was acquired. The polarograph (Radiometer model PO-4) was used with a SCE and a hanging mercury drop cathode. These voltammetric measurements were made as a simple precautionary measure to establish the range of electrode potential over which it

could be ascertained that no Faradiac processes occurred. Hence all capacitance and interfacial tension data reported in the thesis can be presumed to correspond to double layer measurements for an ideally polarized mercury electrode in electrochemically inactive electrolytes within the prescribed stages of potential as discussed for each individual case investigated.

E. Apparatus

1. Electrochemical Cells

For capacitance, interfacial tension and streaming potential work, glass cells of slightly different design were used. These were constructed with a thermostat jacket through which water was circulated from a Haake thermoregulator. Temperature was controlled at $25.0 \pm 0.1^\circ$. A small amount of sodium dichromate was added to the circulating water to minimize the build-up of a static charge or algae formation on the glass in the thermostat jacket.

The cell used for capacitance and streaming potential experiments is shown in figure (9). Mechanical vibrations transmitted through the floors and laboratory benches were a serious problem, because they caused oscillations of the small drop of mercury used for a working electrode. To reduce such vibrations the cell was mounted on a plywood table provided with shock absorbers and stabilized with about 50 kg of lead.

Through the cell top, a capillary tube and working electrode were supported by ground glass joints. A teflon spoon entered through a small hole in the top. The spoon was used to transfer drops of mercury from the capillary to the working electrode. These

Figure 9. Schematic diagram of the electrochemical cell used for capacitance measurements.

electrodes are described below. Via a two-way stopcock, nitrogen gas could be either bubbled through the electrolyte or directed over its surface. Used mercury and electrolyte were drained from the cell through the teflon stopcock at the bottom. Cell volume was about 250 ml. The counter electrode was fitted in a side arm through a 19/38 ground glass joint. For capacitance studies a SCE served the dual purposes of reference and counter electrode. The fritted glass disc was medium porosity, thus permitting a low resistance electrical contact between SCE and the test solution, but minimizing diffusion between compartments. An agar-salt bridge was not employed for fear of introducing contaminants.

In some aspects, the electrochemical cell used in electrocapillary studies differed from the one just described. It was larger and required 500 ml of test solution. The side arm, holding the large SCE was isolated from the main cell compartment by a precision-ground stopcock. A double optical flat was built into the front of the chamber to provide an undistorted view of the capillary tip. A binocular stereo zoom microscope (Bausch and Lomb) of variable magnification (15x to 30x) was employed for observing the mercury position in the capillary. The cap of the cell was designed to accommodate the mercury reservoir-capillary assembly and platinum counter electrode.

2. Electrodes

(a) Saturated Calomel Electrode (SCE)

For capacitance experiments, the electrical instrumentation

was designed for a two electrode configuration, so the counter electrode also had to serve as reference. The SCE was housed in a separate chamber as shown in figure (9). It was built so as to have a very large surface area and low resistance. In the event that it was accidentally polarized, the large area would prevent the potential from being driven too far from its equilibrium value. The low resistance capability has been discussed above. A small volume of mercury (2 ml) in the base of the chamber was covered with a thick layer of calomel (Hg_2Cl_2) paste. A solution of saturated KCl was then poured over the paste along with an abundance of KCl salt crystals, which were also placed in close proximity of the fritted glass disc. The glass tube, with a platinum wire sealed into its end, was then forced into the chamber to make electrical contact with the mercury. Electrodes of this type were very rugged, stable and reliable. The potential was checked frequently against other standards and was found to remain within 0.1 mV of its reversible electrode potential.

(b) Hanging Mercury Drop Electrode (HMDE)^{75,76}

This was the working electrode used in all capacitance studies and can be seen in figure (9). A short piece of new platinum wire (1 cm length, 0.025 cm diameter) was sealed into a section of soft glass tubing (inner diameter of 4 mm). The molten glass was pulled to a thickness of about 1 mm in the region of the glass to platinum seal and then cut on an emery wheel. This was ground with fine emery paper followed by cerium oxide powder until a very smooth surface was obtained. Observation under a microscope (30x magnification) revealed that the glass to platinum seal was intact. Cleaning

took place in aqua regia ($\frac{1}{2}$ hour) followed by hot concentrated nitric acid, and later rinsing in distilled water.

The platinum surface was then plated with mercury by cathodic electrolysis in a pool of mercury covered by 1M perchloric acid. The polarizing current was held constant at 10 mA. Following hydrogen gas evolution for ten minutes from the exposed platinum surface, it was dipped in the mercury for a 15 sec. interval. Polarization, first in the acid solution, then in the mercury, was continued for ten to twelve cycles. When the current was stopped the coated platinum was held in the mercury pool. The resulting mercury film adhered so strongly to the platinum that drops up to 0.06 cm^2 in surface area could be hung with great ease on the electrode.

(c) Drop Delivery System

Mercury drops of accurately known surface area were required for the HMDE. These were formed at the tip of a specially made capillary tube and transferred on a teflon spoon to the HMDE. Figure (9) shows the capillary tip and HMDE in the electrochemical cell. The entire drop delivery system is depicted in figure (10). It consisted of a micrometer drum (Moore and Wright, model 480M) and teflon plunger fitted to the barrel of a syringe (Agl'a Syringe, Burroughs Wellcome and Co.). The syringe was joined to a length of 0.05 cm diameter capillary tubing. The base of the Agl'a syringe was of uniform cross section, $20.00 \text{ mm}^2 \pm 0.02 \text{ mm}^2$, as claimed by the manufacturer and confirmed by calibration with mercury. The teflon plunger had to be machined to fit snugly in the syringe

Figure 10. Mercury drop delivery system.

barrel. This provided leak-proof operation and little friction. The capillary tube was mounted on the cap of the cell as shown in figure (9). The micrometer drum was clamped into position on the rigid framework which also was used to support the electrochemical cell.

The end of the capillary tube was slightly tapered to about 0.015 cm internal diameter. Before joining the Agla syringe, the capillary tubing was first given a coating of silicone by drawing vapours of dimethyldichlorosilane under partial vacuum up the bore of the capillary. This was followed by steam treatment and thorough rinsing in distilled water. The silicone coating was cured by heating in an oven at 150° for twelve hours. The purpose of siliconizing was to prevent wetting of the capillary by water which would have caused difficulties in reproducing mercury drops of uniform size.

Considerable caution had to be exercised when filling the drop delivery system to ascertain that no trapped air was included. The capillary tip was lowered into a beaker of mercury and the teflon plunger slowly withdrawn to pull mercury up through the capillary. The syringe was lowered to a position below the capillary tip permitting mercury to siphon through the system. The plunger was replaced to force the mercury back into the beaker; then partially withdrawn to suck in more mercury. This cycle was repeated in such a manner as to create a partial vacuum in the capillary and syringe, thereby removing trapped air. Finally the plunger was carefully forced into the barrel and the system inspected for entrapped air. If no air was present, drops could be removed from the capillary

tip and the mercury thread would not fluctuate over a long period of time.

Drop area was calculated from the calibrated micrometer drum and syringe diameter, assuming a spherical drop. The area of mercury-coated platinum cross-section was also taken into account. The error in calculated surface area varied with drop size:

Drop Area	Error
0.010 cm ²	± 2%
0.030 cm ²	±0.5%
0.060 cm ²	±0.2%

The drop size generally employed for capacitance studies was 0.041 cm², corresponding to a rotation of the micrometer drum through 0.040 mm.

3. Chemical Reagents and Other Materials

(a) Water Purification

The differential capacitance technique is very sensitive to impurities present in solution. The use of HMDE presents a problem, because of the relatively long time during which the mercury surface is exposed to the solution. Impurities can, within a long period of time, diffuse to the electrode where adsorption may occur to such an extent as to vitiate the intended measurements. This is a crucial problem due to the high adsorbability of many organic substances which, if present in only trace amounts (eg. less than 10⁻⁶ mol l⁻¹), can drastically alter the structure of the e.d.l. For these reasons special precautions had to be taken to purify water.

The Chemistry Department supplies water which has been distilled once in a Barnstead still and stored in large tin-lined tanks. The conductivity of this distillate is usually less than 2×10^{-6} ohm⁻¹ cm⁻¹ (ie. μ mho cm⁻¹) at 23°, measured with a simple conductivity cell (solu Bridge, model RD-B3). The ionic content is therefore quite small, but organic impurity levels are too high for use in double layer studies. This water was distilled a second time in a continuous distillation apparatus (Corning Still, model AG2) to which alkaline permanganate solution was added. The still could be operated in this manner for only four to six hours due to deterioration in the boiling characteristics of the quartz heating element. The distillate was collected in a large bottle (capacity about 20 l) which had been in use for this purpose for eight to ten years. A third distillation from alkaline permanganate was then done by a batch process and resulted in a very good quality of water. The conductivity was always less than 1μ mho cm⁻¹ and had a pH in the range 6.1 to 6.5. Solutions for capacitance work were made from the triply distilled solvent, but for most other requirements the doubly-distilled water was found to be of sufficient purity.

(b) Mercury

High quality mercury is supplied by the Chemistry Department. The purification methods are similar to those advocated by Ives and Janz⁷⁷ and Meites⁷⁸. This mercury was stored under dry nitrogen in pyrex bottles and could be kept for several months without appreciable scum formation. Before use, a final Hulet type distillation was done under partial vacuum, allowing a small ingress of filtered air below the surface of the boiling mercury.

(c) Electrolyte Solutions

For double layer studies, solutions were prepared at 25° by dissolving weighed quantities of the appropriate chemicals in purified water. Only highest purity grades of commercially available reagents were used; these were either Fisher "certified" or British Drug Houses "Analar" brands.

For viscosity and density measurements, stock solutions were prepared by dissolving 0.50 moles of the salt in doubly distilled water and making up to the mark in 1000 ml. volumetric flasks at $25.0 \pm 0.1^\circ$. The stock was diluted in the correct proportions to make solutions of concentrations: 0.005, 0.010, 0.020, 0.030, 0.040, 0.050, 0.0625 and 0.100M. For Li_3Cit and K_3Cit solutions, 0.50 moles of citric acid were used and appropriate base added to pH = 8.81 and pH = 9.97, respectively. The LiOH was made approximately 4M, and KOH , 7.5M. Dilutions were made as above. Viscosity studies were also done for sodium-citrate solutions of different pH: 3.90, 4.50, 5.25 and 5.50. These solutions were prepared by adding NaOH to citric acid and making to 0.50M, then diluting as required.

(d) Nitrogen Gas

Nitrogen was Linde Co. certified grade. Oxygen was removed by bubbling through a solution of vanadous chloride over zinc amalgam as specified by Meites⁷⁸. The gas was then passed through triply distilled water in two separate gas washing bottles, after which it entered a third empty bottle to allow entrained water droplets to fall out. Samples of the distilled water were periodically checked for conductivity changes to detect any carry-over of possible

contaminants from the oxygen scrubber. The nitrogen gas, now saturated with water vapor, was then used for deaerating the test electrolyte in the electrochemical cell or as a cover gas to maintain a small positive pressure.

All solutions were saturated with N_2 gas before measurement of either interfacial tension or capacitance. This was done to remove dissolved oxygen or carbon dioxide, because both gases are known to decrease the mercury-water interfacial tension. Dissolved oxygen and carbon dioxide from a typical air sample (0.27 mm of CO_2) lower γ by 40 to 50 mNm^{-1} (ref. 127).

(e) Glassware

Electrochemical cells, volumetric flasks and all other glassware (except viscometers) were cleaned in a 1:1 mixture of concentrated nitric-sulphuric acid for about one hour. Hot tap water was then flushed over the glass for ten minutes, followed by thorough rinsing in distilled water. Cells and flasks were filled with doubly distilled water and left to soak for several hours before use. Conductivity measurements were made to ascertain removal of all acid by the rinsing procedure.

For double layer studies the cells were rinsed twice with solution before filling up for the actual run. Since experiments proceeded from most dilute to concentrated solutions, rinsing with the next solution was considered adequate and the elaborate cleaning process was only done when the electrolyte system was changed.

F. Computational Methods

Data from interfacial tension and capacitance experiments were processed by computer programming methods on a Zerox Sigma Seven digital computer. Separate programs were used for processing each type of data although the numerical methods employed for analysis were in some cases common to both programs. To maintain clarity of presentation an outline of the separate treatments will be given.

Electrocapillary curves were fitted to fifth, sixth and seventh order polynomials by the least squares method. The standard deviation of the original data from that produced by the polynomial was calculated and comparisons made for the order of the fitting curve. The seventh order polynomial was found to best represent the data in all cases. First and second derivatives were calculated to give the electrode charge, q_m , and capacitance, C , respectively (see equations (7) and (15)). Third order Lagrangian interpolation⁷⁹ was applied to γ , E_+ data to calculate these variables at constant integral values of q_m . The program then computed the function, $\xi_+ = \gamma + q_m E_+$, for all integral q_m for each electrolyte concentration (C). These values of ξ_+ , q_m and C were then punched on computer cards. These cards were submitted in a second program and the computer evaluated the relative surface excess of anions by fitting a polynomial to ξ_+ , $\ln a_{\pm}$ data at integral q_m , according to equation (14). The standard deviation in ξ_+ was used as the criterion for determining the correct polynomial, which invariably was found to be third or fourth order for the electrolytes studied.

Capacitance data, obtained from recorder traces, were fed to

the computer in two evenly spaced potential intervals of: 25 mV positive to the p.z.c. and 50 mV on the negative side. Two integrations were performed on these data: first to calculate q_m and second for the interfacial tension (γ_c). The subscript "c" is used to distinguish this value from the directly measured interfacial tension, γ . The first integration steps, either side of the p.z.c., were done using the trapezoid rule, because the intervals of potential were generally not equal in size to the evenly spaced intervals. After the first step all subsequent integration was done by Simpson's rule. Interpolation was by the same numerical method as for electrocapillary data. At constant, integral q_m the following interpolated variables were calculated: electrode potential (E_+), interfacial tension (γ_c), integral capacitance (K) and the reciprocal capacitance (C^{-1}). Results were printed only for those values of q_m which were common to all solution concentrations. Relative surface excess of the anion was calculated as described above. All these operations carried out on capacitance data were made using a single computer program. The full details of similar computer calculations have been published previously¹¹⁵.

CHAPTER IVRESULTSA. Reliability of Double Layer Data1. Capacitance Curves

The accuracy of capacitance data, obtained with the automatic recording technique is demonstrated in figure (11). Results are shown for 0.05M K_2SO_4 at 25°. The points are impedance bridge results of Grahame et al.⁸⁰ for dropping mercury electrode, and the solid line represents data obtained by the author using the HMDE. Discrepancies were less than $0.5 \mu F cm^{-2}$ over most of the capacitance curve. Larger differences at most positive potentials are attributed to the HMDE which is more susceptible to accumulation of impurities than is the dropping mercury electrode. Results of comparable accuracy were found in experiments done in other solutions: 0.10M and 1.0M KCl and HCl, 0.10M $NaClO_4$ and 0.10M Li_2CO_3 . An analysis was made to ascertain the reproducibility of capacitance curves for 0.10M solutions of trisodium citrate (Na_3Cit), for which no literature data were available for comparison. In figure (12) the data for four representative runs are shown, and the different electrode areas are indicated by their respective plotting symbols. The smooth curve describes the average of a total of twenty runs. The overall accuracy, as determined from this study, was: $\pm 0.4 \mu F cm^{-2}$ in the region of the capacitance hump ($E \approx -0.3$ volts), $\pm 0.8 \mu F cm^{-2}$ for the portion of the curve either side of the p.z.c., where capacitance varies strongly with potential, and $\pm 0.4 \mu F cm^{-2}$ at negative potentials where C ranges from 15 to 20 $\mu F cm^{-2}$. These error values are considered quite tolerable for the

Figure 11. Comparison of capacitance data for 0.05M K_2SO_4 . Points taken from ref. 80; (—) present work.

Figure 12. Reproducibility of capacitance data for 0.10M trisodium citrate solutions. Drop area of HMDE: Δ, O (0.041 cm^2), $x, \bullet$ (0.034 cm^2). (—) average capacitance curve.

interpretation of the double layer results¹¹⁶.

2. Electrocapillary Curves

Interfacial tension data were generally repeatable to $\pm 0.02 \text{ mNm}^{-1}$ near the e.c.m. and to about $\pm 0.06 \text{ mNm}^{-1}$ on the descending branches of electrocapillary curves. The main sources of error are due to small uncertainties in electrode potentials and manometer height readings. In chapter V other effects will be described when comparison is made between directly measured interfacial tension and those derived from twice-integrated capacitance values.

3. Double Layer Results

For all systems studied, the results of electrocapillary and capacitance work will be given together with related discussions and interpretation in the chapters to follow. It is anticipated that such a format will contribute to better continuity and convenience for the reader. It should reduce the need to constantly return to the results chapter for consulting tables and diagrams referred to in the text.

B. Results of Viscosity Studies

Viscosity results are shown in figure (13) for Li_3Cit , Na_3Cit and K_3Cit at 25° . In these solutions the pH varied from 8.1 to 9.4 over the concentration interval: 0.005M to 0.10M. Data are plotted according to the Jones-Dole⁴² equation and the straight lines in figure (13) follow an order related to the magnitude of the B-

Figure 13. Plot of Jones-Dole equation for aqueous solutions of: (a) $\text{Li}_3\text{Cit.}$, (b) $\text{Na}_3\text{Cit.}$ and (c) $\text{K}_3\text{Cit.}$ at 25.0°C .

coefficient for the cation. This particular part of the study was made to examine the relative order of ion-ion and ion-solvent interactions, in view of the differences reported for ion-pair formation constants. The published values⁵⁴ of these constants are given in column 7 of Table I. Also listed, are the experimentally determined intercepts (A) and slopes (B) of the Jones-Dole equation. Values are given for the A-coefficient (A_{calc}) as calculated by an equation of Falkenhagen and Vernon (see ref. 81a). The B-coefficient for each salt solution was separated into its ionic parts on the basis of two assumptions: (1) that MCit^{2-} ion-pairs were the only anionic species in solution (column 6) and (2) that all anions were Cit^{3-} (column 5).

In figure (14) Jones-Dole plots are given for sodium-citrate salts at widely differing pH. The slopes (B) and intercepts (A) are contained in Table II, columns two and three. The solutions with pH = 5.5 are for di-sodium citrate. By separation of the B-coefficient the value for the HCit^{2-} ion $B(\text{HCit}^{2-})$ was estimated to be 0.59. Similarly at pH = 3.9, which corresponds to a solution of mono-sodium citrate, the ionic B-coefficient was estimated as $B(\text{H}_2\text{Cit}^-) = 0.46$ (see Table II, column four). The above values are approximations, due to the fact that citrate solutions are composed of a variety of anionic species (see Chapter VI section B). Results for Na_3PO_4 are plotted in figure (15) and some data are shown for the mono- and di-sodium salts. The values for Na_2HPO_4 and NaH_2PO_4 were taken from the literature⁷⁴ and are included for comparison with Na_3PO_4 . Anionic B-coefficients, calculated from the slopes of lines in figure (15), were: 0.619 (PO_4^{3-}), 0.48 (HPO_4^{2-})

TABLE I Results of Viscosity Measurements at 25°C for Alkali Metal Citrate Salts

Electrolyte	$A^{(b)}$ (1/mol) ^{1/2}	$B^{(b)}$ (1/mol)	$A_{calc}^{(a)}$ (1/mol) ^{1/2}	$B_{Cit^{3-}}^{(c)}$ (1/mol)	$B_{MCit^{2-}}$ (1/mol)	K_f (1/mol)
Li_3Cit	0.042 ±0.004	1.057 ±0.024	0.0345	0.608	0.758	6.8±0.1
Na_3Cit	0.036 ±0.008	0.873 ±0.045	0.0321	0.614	0.700	5.0±0.1
K_3Cit	0.027 ±0.004	0.615 ±0.022	0.0287	0.636	0.629	3.9±0.1

(a) $\lambda^0 = 70 \text{ mho} \cdot \text{cm}^2$ for Cit^{3-} (ref. 74)

(b) Errors are 95% confidence limits; A and B were evaluated by the least squares fit method.

(c) $B(Li^+) = 0.150$, $B(Na^+) = 0.086$, $B(K^+) = -0.007 \text{ (1 mol}^{-1}\text{)}$ (ref. 44).

Figure 14. Plot of Jones-Dole equation for aqueous solutions of sodium-citrates at different pH values: (a) $\text{Na}_3\text{Cit.}$, pH= 8.1 to 8.8, (b) $\text{Na}_2\text{HCit.}$, pH= 5.5, (c) pH=5.25, (d) pH= 4.5, (e) pH= 3.9 and (f) citric acid, pH= 2.5 . $T = 25.0^\circ\text{C}$.

TABLE II Results of Viscosity Measurements at 25⁰ for Sodium-Citrate Solutions at Different pH.

pH	A (l/mol) ¹¹²	B (l/mol)	B (Anion) (l/mol)
3.9	0.01	0.55	0.46 (H ₂ Cit ⁻)
4.5	0	0.71	---
5.25	0.01	0.76	---
5.5	0.02	0.76	0.59 (HCit ²⁻)
8.1 to 8.8	0.036±0.008	0.87 ³ ±0.04 ⁵	0.61 (Cit ³⁻)

Figure 15. Plot of Jones-Dole equation for aqueous solutions of:
 (a) Na_3PO_4 , (b) Na_2HPO_4 (ref. 74) and (c) NaH_2PO_4 (ref. 74) at 25.0°C .

and 0.31 (H_2PO_4^-). The experimentally determined A-coefficient for Na_3PO_4 was 0.014; for the other salts mentioned above they were approximately zero.

Viscosity was measured for 0.10M Na_3Cit as a function of temperature at five degree intervals from 5° to 45° . The results are shown in figure (16), in which $\ln \eta$ is plotted against the reciprocal of temperature. The viscosity η was calculated from the measured relative viscosity (η/η_0) and viscosity-temperature data reported by Korson et al.⁸² for pure water. The activation energy for viscous flow, $\Delta E^\ddagger$ was obtained from the slope in figure (16) (equation 31). At 25° the computed value for $\Delta E^\ddagger$ was $4129 \text{ cal mol}^{-1}$, which gave for the Cit^{3-} ion $\Delta E^\ddagger_- \approx 100 \text{ cal mol}^{-1}$. In applying equation (32) at 25° the following were used:

$$\Delta E^\ddagger_0 = 3963 \text{ cal mol}^{-1} \text{ (ref. 82) and } \Delta E^\ddagger_+ = 20 \text{ cal mol}^{-1}$$

for the sodium ion⁴³.

C. Results of Density Measurements

For the lithium, sodium and potassium salts of citric acid fairly precise density measurements were obtained at 25° over the concentration interval from 0.005M to 0.100M. In other systems examined the data were only precise enough to use for calculation of the relative viscosities. Data were found to best fit an equation of the form:

$$(D - D_0)^{1/2} = k_1 + k_2 C^{1/2} \quad (52)$$

In equation (52), k_1 and k_2 are constants whose values are listed in Table III. The molar concentration is C and D is the solution density.

Figure 16. Temperature dependence of solution viscosity for 0.10M trisodium citrate.

TABLE III Constants of Equation (52) For Citrate Salts at 25.0°

Electrolyte	$k_1 \times 10^3$	k_2	S.E. $\times 10^5$	n
Li ₃ Cit	2.93	0.35939	5.6	8
Na ₃ Cit	2.46	0.42025	7.3	9
K ₃	2.78	0.44152	8.0	8

For pure water at 25.0° D_0 was taken as 0.99708 g ml⁻¹ (ref. 74). Density data were fitted to equation (52) by the least squares method and the standard error of the estimate, S.E., was evaluated and is listed in column four. The number of solution concentrations used in the least squares analysis is n.

$$S.E. = \left(\frac{\sum \delta_i^2}{n} \right)^{1/2}$$

where $\delta_i = D_i - D_{calc}$ and D_{calc} is the density value calculated from equation (52) using least squares constants k_1 and k_2 . These results were used to calculate ionic partial molal volumes and will be discussed later.

CHAPTER VDOUBLE LAYER STUDY OF PHOSPHATE
SOLUTIONSA. Results of Double Layer Studies

The sodium salts of orthophosphoric acid present the double layer electrochemist with the interesting possibility of comparing the adsorption behavior of ions of very similar structure, but carrying different charges: H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} . It is also a challenging problem to attempt to apply the theoretical calculations of the Gouy-Chapman-Stern model for the double layer to non-symmetrical electrolytes such as Na_2HPO_4 and Na_3PO_4 . Parsons and Zobel²² have already studied aqueous solutions of NaH_2PO_4 at the mercury electrode over the concentration range: 0.01M to 6M, using electrocapillary and capacitance data. Their results are of direct interest to the present work, because they provide a basis for comparing the double layer measurements and calculations obtained for Na_2HPO_4 and Na_3PO_4 . All references made in this discussion to the adsorption behavior of NaH_2PO_4 are derived from the above mentioned paper by Parsons and Zobel²², and some of their more important results will be reproduced here in order to make direct comparison with results obtained for Na_2HPO_4 and Na_3PO_4 . Some of the experimental and theoretical difficulties encountered in the study of NaH_2PO_4 (ref. 22) are also common to the other two phosphate salts described in this chapter. However, in at least two particular cases the double layer results obtained for Na_2HPO_4 and Na_3PO_4 are distinctly different from those observed by Parsons and Zobel²² for NaH_2PO_4 , and these are discussed at some length below in sections B and C.

The results in Tables IV and V are for aqueous solutions of Na_2HPO_4 and Na_3PO_4 , respectively. The potential of zero charge, measured versus a SCE by the streaming mercury electrode method (Chapter III.D) is tabulated in column two ($E_{(\text{SCE})}^{\text{p.z.c.}}$). The p.z.c. and all other potentials were converted to the thermodynamic scale of the sodium ion electrode by measuring the potential difference between a SCE and a calibrated Na^+/Na glass electrode in the various solutions investigated. These p.z.c. values are given with respect to the Na^+/Na electrode in column three ($E_{(\text{Na}^+/\text{Na})}^{\text{p.z.c.}}$). Results for $E_{(\text{SCE})}^{\text{p.z.c.}}$ were accurate to within ± 0.1 mV or less in all solutions, except for 0.0025M Na_2HPO_4 and 0.001M Na_3PO_4 . Errors for the latter solutions were about ± 0.5 mV. The potential differences measured between the SCE and Na^+/Na electrode were only accurate to ± 0.5 mV. Mean molal activities, $a_{\pm}$, were calculated according to equations for unsymmetrical electrolytes²¹, using mean molal activity coefficients from Scatchard and Breckenridge⁸³. For solutions more dilute than 0.1 molal, activity coefficients were extrapolated using the Debye-Huckel limiting law. Corrections were made to adjust activities to the molar concentration basis.

Differential capacitance at the p.z.c., $C^{\text{p.z.c.}}$, is given in column four. For Na_2HPO_4 solutions the interfacial tension maximum, γ^{max} , was determined from data published by Gouy⁸⁴, who reported only a single datum value ($c = 0.5\text{M}$), but gave several points for the salt, K_2HPO_4 over a wide range of concentrations (0.1M to 7.74M). The values of γ^{max} listed in Table IV, column five, were calculated by assuming a linear dependence of γ^{max} on concentration, equal to the variation exhibited by γ^{max} in K_2HPO_4 solutions between

TABLE IV Double Layer Parameters For Na_2HPO_4 at 25°

conc.	$-E_{(\text{SCE})}^{\text{p.z.c.}}$	$-E_{(\text{Na}^+/\text{Na})}^{\text{p.z.c.}}$	$C^{\text{p.z.c.}}$	γ^{max}	pH
(mol l ⁻¹)	(mV.)	(mV.)	($\mu\text{F cm}^{-2}$)	(mNm ⁻¹)	(± 0.02)
0.0025	431.0 $\pm$ 0.5	---	11.8	---	8.94
0.005	431.5	442	13.3	426.7	9.13
0.010	432.0	459	16.1	426.7	9.20
0.020	431.6	472	18.0	426.7	9.26
0.040	431.3	487	20.1	426.8	9.27
0.050	431.2	495	20.6	426.8	9.24
0.10	429.7	507	21.8	426.8	9.20
0.20	431.0	525	23.0	426.9	9.11
0.50	430.1	539	24.7	427.2	8.96

TABLE V Double Layer Parameters For Na_3PO_4 at 25°

conc.	$-E^{\text{p.z.c.}}_{(\text{SCE})}$	$-E^{\text{p.z.c.}}_{(\text{Na}^+/\text{Na})}$	$C^{\text{p.z.c.}}$	γ^{max}	pH
(mol l ⁻¹)	(mV.)	(mV.)	($\mu\text{F cm}^{-2}$)	(mNm ⁻¹)	(± 0.02)
0.001	429.0 $\pm$ 0.5	433	10.0	---	---
0.0025	428.8	455	13.2	426.8	11.36
0.005	429.7	474	15.4	426.8	11.63
0.010	430.2	488	18.1	427.6	11.86
0.020	430.6	507	20.5	427.4	12.00
0.050	430.4	525	22.0	427.8	12.22
0.10	431.2	540	24.1	427.5	12.42
0.20	431.9	555	24.9	427.7	12.55
0.50	431.7	571	25.9	427.8	12.86

0.10M and 1.0M.

For Na_3PO_4 solutions experimental values of γ^{max} are reported in Table V. Gouy⁸⁴ reported $\gamma^{\text{max}} = 428.0 \text{ mNm}^{-1}$ for Na_3PO_4 (1M), which compares favorably with the present study for $c = 0.50\text{M}$. Since Na_3PO_4 is soluble only to about $c = 0.7\text{M}$ at 25° , the Gouy⁸⁴ concentration of $c = 1\text{M}$ may be a misprint, or the result of uncertainty regarding the particular crystal hydrate of trisodium phosphate involved.

B. Morphology of Capacitance Curves

Differential capacitance curves for a range of concentrations of Na_2HPO_4 and Na_3PO_4 are shown in figures (17) and (18), respectively. These plots are very similar in shape and comparable to those for NaOH reported by Payne²⁶. Neither Na_2HPO_4 nor Na_3PO_4 curves had a capacitance hump. This result was carefully verified by recording the capacitance curves up to about $200 \mu\text{F cm}^{-2}$, but data are not reported beyond $50 \mu\text{F cm}^{-2}$ because the Kowalski-Srzednicki method does not produce sufficiently accurate quantitative results at such large capacitances. The absence of a capacitance hump was additionally confirmed by comparison with impedance bridge measurements for a 0.10M solution of Na_2HPO_4 obtained by other workers⁸⁵. Aqueous solutions of Na_3PO_4 are very alkaline, so the absence of the hump is not unexpected in view of the fact that no hump has been reported for capacitance curves at the mercury-NaOH interphase²⁶ (see also figure (19)). However, Parsons and Zobel²² showed capacitance results for 0.015M, 0.10M and 1.0M solutions of NaH_2PO_4 in which a capacitance hump is

Figure 17. Capacitance curves for Na_2HPO_4 solutions: (a) 0.005M, (b) 0.010M, (c) 0.020M, (d) 0.040M, (e) 0.050M, (f) 0.10M, (g) 0.20M and (h) 0.50M.

Figure 18. Capacitance curves for Na_3PO_4 solutions: (a) 0.001M, (b) 0.0025M, (c) 0.005M, (d) 0.010M, (e) 0.020M, (f) 0.050M, (g) 0.10M, (h) 0.20M and (j) 0.50M.

clearly depicted. In figure (19) their results are shown for 0.10M NaH_2PO_4 .

One of the major experimental difficulties in the present work (and also in Payne's study²⁶ of NaOH) was the very rapid increase of capacitance at anodic potentials which imposed a limit beyond which accurate data could not be obtained. Thus it was not possible to record capacitance curves for Na_2HPO_4 for $q_m > 8 \mu\text{C cm}^{-2}$ or more positive than $6 \mu\text{C cm}^{-2}$ for Na_3PO_4 . Payne's results²⁶ were similarly restricted to $q_m < 6 \mu\text{C cm}^{-2}$ for NaOH, however electrode charge values up to $20 \mu\text{C cm}^{-2}$ were reported²² for NaH_2PO_4 . The limits of anodic polarization are shown in figure (19) in which capacitance curves have been drawn for Na_2HPO_4 (0.04M) and Na_3PO_4 (0.02M). These are compared with published curves for NaH_2PO_4 (0.10M)²² and NaOH (0.10M)²⁶ on the same graph. The electrode potential scale in figure (19) is with respect to a SCE (ie. a constant activity reference electrode) and the capacitance data are for solutions of approximately equal ionic strength (0.1 mol l^{-1}). Inspection of figure (19) shows that the steeply rising portion of the capacitance curves occurs towards more anodic potentials in the order: Na_3PO_4 , NaOH, Na_2HPO_4 , NaH_2PO_4 . It has been suggested that the rapid increase of capacitance in NaOH is due to hydroxyl ion specific adsorption preceding the formation of mercuric oxide²⁶. It is claimed that capacitance curves for NaOH asymptotically approach the potential at which mercury is reversibly oxidized to mercuric oxide²⁶.

Impedance measurements by Armstrong and co-workers^{27,28} have shown that mercury, anodically polarized in NaOH, dissolves as

Figure 19. Capacitance curves for: (a) 0.1M NaOH, $\text{pH} \approx 13$ (ref. 26), (b) 0.10M NaH_2PO_4 , $\text{pH} \approx 4.7$ (ref. 22), (c) 0.040M Na_2HPO_4 , $\text{pH} = 9.27$ and (d) 0.020M Na_3PO_4 , $\text{pH} = 12.00$.

$\text{Hg}(\text{OH})_2$ at such a rate that the exchange current is too large to be measured. The double layer capacitance simultaneously increases rapidly as the reversible mercuric oxide potential is approached. In figure (19) the reversible mercuric oxide potential for 0.10M NaOH occurs at -0.083 volts on the SCE scale.

$$E = 0.684 - 0.059 \text{ pH (vs. SCE)} \quad (53)$$

If it is assumed that the rapid increase of anodic capacitance in Na_2HPO_4 and Na_3PO_4 solutions is also controlled by the presence of hydroxyl ions, then the potential at which this should occur may be calculated directly (equation (53)) from measured pH values (Tables IV and V). The relative positions of the curves of figure (19) for 0.04M Na_2HPO_4 (pH = 9.27) and 0.02M Na_3PO_4 (pH = 12.00) may be compared with 0.10M NaOH (pH = 13.0) on the basis that the reversible mercuric oxide electrode potential changes by -0.059 volts for unit increase in pH at 25°. Where the capacitance rise is steep, (taking $C = 42 \mu\text{F cm}^{-2}$ in figure (19)) the curve for Na_2HPO_4 should occur 0.220 volts positive of the NaOH curve and the Na_3PO_4 curve should be displaced 0.059 volts from the NaOH curve. The actual positions are 0.030 volts and -0.035 volts for the Na_2HPO_4 and Na_3PO_4 curves, respectively, relative to the capacitance curve for NaOH. The results of these calculations suggest little control by hydroxyl ions of the rapidly rising anodic capacitance.

The situation can be clarified somewhat by examining changes in solution pH as a function of concentration. First, for Na_3PO_4 , the anodic capacitance, when plotted on the SCE potential scale, shifted to more negative potentials with increasing concentration (and increasing pH; see Table V). At $C = 42 \mu\text{F cm}^{-2}$ the change in potential was a linear function of the solution pH (-0.019 volts

per unit increase in pH). This observed shift in potential was only about one-third (ie. $0.019/0.059$) of that expected if hydroxyl ions alone controlled the rise in the anodic capacitance. In Na_2HPO_4 solutions there was considerably less variation of the pH over the concentration range studied, (see Table IV), so no meaningful correlation could be established for the shift in the potential of the anodic capacitance rise with the change in the reversible HgO electrode potential.

Since H_3PO_4 is a tribasic acid, it is important to consider the relative proportions of the various species of anion present in sodium-phosphate salt solutions. The approximate anion concentrations are listed in Table VI for tenth-molar aqueous sodium-phosphate salt solutions. The values given in Table VI were taken from a logarithmic concentration -- pH diagram⁸⁶ for the phosphoric acid -- phosphate salt system, which is shown in figure (20). Calculated pH values in Table VI agree favorably with measurements in the present work as listed in Tables IV and V. It is interesting to note, according to Table VI and figure (20), that solutions of Na_3PO_4 are composed of almost equal proportions of the anions: HPO_4^{2-} , PO_4^{3-} and OH^- , while in Na_2HPO_4 solutions only the HPO_4^{2-} ion is present to any significant amount. Therefore, both disodium hydrogen phosphate and trisodium phosphate solutions contain appreciable amounts of the divalent anion, HPO_4^{2-} . Ives and Janz⁷⁷ have reported that mercurous ions in the presence of phosphoric acid produce a white precipitate, Hg_2HPO_4 , with a solubility product¹³⁹ of 10^{-12} . However, when mercurous ions are added to either NaH_2PO_4 or Na_2HPO_4 solutions only a yellow insoluble substance, presumably

TABLE VI Ionic Composition of 0.1 Molar Sodium-Phosphate Salt Solutions

Salt	pH	IONIC CONCENTRATIONS (mol l ⁻¹)			
		H ₂ PO ₄ ⁻	HPO ₄ ²⁻	PO ₄ ³⁻	OH ⁻
NaH ₂ PO ₄	4.72	0.1	~ 5 × 10 ⁻⁴	~ 0	~ 0
Na ₂ HPO ₄	9.72	5.9 × 10 ⁻⁵	~ 0.1	2.7 × 10 ⁻⁴	5.6 × 10 ⁻⁵
Na ₃ PO ₄	12.60	2.2 × 10 ⁻⁷	4 × 10 ⁻²	6.9 × 10 ⁻²	4 × 10 ⁻²

Figure 20. Logarithmic concentration diagram for 0.10M phosphoric acid or phosphate salt solutions (from ref. 86, p.218).

$(\text{Hg}_2)_3(\text{PO}_4)_2$ is found⁷⁷. Although not mentioned by Ives and Janz, it is quite probable that the white precipitate is also formed in the latter situation. It is therefore reasonable to suggest that the rapid rise of the anodic capacitance observed for mercury electrodes in Na_2HPO_4 and Na_3PO_4 is due to the adsorption of the HPO_4^{2-} ion which may ultimately result in the formation of $(\text{Hg}_2)_3(\text{PO}_4)_2$ at very positive electrode potentials. However, one may not discount the possibility of forming Hg_2HPO_4 and HgO , the latter⁸⁸ being more favorable in Na_3PO_4 solution as noted by Lingane, because the HgO reversible electrode potential becomes sufficiently negative in alkaline solution (see equation (53)).

C. The Capacitance Hump

Payne²⁶ has shown that the capacitance hump in NaF solutions can be eliminated by increasing the pH beyond a nominal value of 10 through additions of small amounts of NaOH. In his study, the steeply rising part of the capacitance curve was displaced to more negative potentials by approximately 0.15 volts. In a related work, Minc and Jastrzebska⁸⁷ noted that in LiCl solutions the value of capacitance at the hump diminished in magnitude with increased pH, until at pH = 12.9 the hump disappeared. At this point the shift of electrode potential was about -0.2 volts.

In the present research, the effect of small additions of NaOH to a 0.10M solution of Na_2SO_4 was studied. The results are graphically presented in figure (21) in which the anodic portion of the capacitance curves is plotted on the SCE scale for the pure Na_2SO_4 solution (pH = 7.76) and those with increased pH. At pH = 11.63 the capacitance hump no longer can be distinguished and the

Figure 21. Anodic part of capacitance curves for 0.10M Na_2SO_4 (pH = 7.76) and 0.10M Na_2SO_4 with added NaOH. Figures with each curve indicate the solution pH.

corresponding shift of the anodic capacitance (taken at $47 \mu\text{F cm}^{-2}$) is -0.063 volts per unit increase of pH. This is within a few millivolts of the expected change for the HgO electrode potential (see equation (53)). The mercuric oxide electrode is reversible to OH^- ions, so it appears that hydroxyl ions cause the shift of anodic capacitance even in the presence of SO_4^{2-} . In the solution with pH = 11.63, the concentration of OH^- is about $4 \times 10^{-3}\text{M}$; ie. only roughly 4% of the sulphate ion concentration. The pH effect in Na_2SO_4 is therefore similar to that observed by Payne in 0.10M NaF (see ref. 26, figure (11)). In the comparison of these latter two systems, the predominant anions are only slightly specifically adsorbed at mercury; F^- is somewhat less specifically adsorbed than is SO_4^{2-} . In the fluoride case, the disappearance of the hump and corresponding shift of anodic capacitance to cathodic potentials take place when the concentration of hydroxyl ions reaches a nominal one percent of the fluoride ion concentration. In fluoride and sulphate solutions the concentrations of OH^- relative to the main anionic species are similar at the point where the hump disappears. This factor is compared in Table VII for these and other aqueous electrolytes in which relatively weak anion specific adsorption occurs on mercury electrodes. In Table VII the Cl^- ion is known to be specifically adsorbed to a somewhat greater extent than either F^- or SO_4^{2-} and in this case a large concentration of OH^- must be used to eliminate the capacitance hump (ie. about 100 times more than required in NaF and Na_2SO_4). Among the salts of polybasic acids, the only one which appears to have a hump in the presence of a relatively large hydroxyl ion concentration is

TABLE VII Apparent Effect of Hydroxyl Ion Concentration on the Capacitance Hump in Various Solutions

Salt	Added Base	pH	$[\text{OH}^-]/[\text{anion}]$	Remarks	Ref.
0.1M LiCl	LiOH	11.4	2.5×10^{-2}	hump	87
0.1M LiCl	LiOH	12.9	0.79	no hump	87
0.1M NaF	NaOH	10	10^{-3}	hump	26
0.1M NaF	NaOH	11	10^{-2}	no hump	26
0.1M Na_2SO_4	NaOH	10.63	4.3×10^{-3}	hump	Present Work
0.1M Na_2SO_4	NaOH	11.63	4.3×10^{-2}	no hump	
0.1M NaH_2PO_4	none	4.7	5×10^{-9}	hump	22
0.1M Na_2HPO_4	none	9.20	1.6×10^{-4}	no hump	Present Work
0.1M Na_3PO_4	none	12.42	0.27	no hump	
0.05M K_2CO_3	none	11.6	8×10^{-2}	shoulder at $C \approx 50 \mu\text{F cm}^{-2}$	80
0.1M KHCO_3	none	8.4	2.5×10^{-5}	broad hump $C \approx 33 \mu\text{F cm}^{-2}$	80

K_2CO_3 ⁸⁰. This may be due to the fact that CO_3^{2-} (or HCO_3^- or OH^-) is more specifically adsorbed on a positive mercury electrode than is SO_4^{2-} , for example²⁹. As will be shown later, there is specific adsorption of HPO_4^{2-} and PO_4^{3-} ions. This factor, together with the effects mentioned above for OH^- in weakly adsorbed anion systems may account for the absence of a capacitance hump in phosphate solutions.

D. Comparison of Electrocapillary and Capacitance Results

Interfacial tension (γ_c) was calculated by double integration of capacitance data, using the computer programming technique described in Chapter III, Section F. Required integration constants were: the potential of zero charge (p.z.c.) and the interfacial tension (γ^{max}), listed in Tables IV and V.

Interfacial tension data were measured (γ_m) only for Na_3PO_4 solutions. Agreement of electrocapillary (γ_m) and integrated capacitance curves (γ_c) was not satisfactory on the anodic branch. Discrepancies were largest for the most dilute solutions ($c < 0.10M$) and amounted to 6.5 mNm^{-1} at extreme positive potentials in 0.005M solution. On the cathodic branch the differences were less than 0.5 mNm^{-1} . Parsons and Zobel²² reported similar problems with NaH_2PO_4 solutions (0.01M and 0.05M), and attributed them to a variation in contact angle between the glass capillary wall and mercury.

When mercury is anodically polarized in a buffered phosphate solution (pH = 6.52) it has been claimed²⁴ that the complex formed in a monolayer on the electrode was Hg_2HPO_4 . Lingane⁸⁸ had

previously suggested that the complex was $(\text{Hg}_2)_3(\text{PO}_4)_2$, which in strongly alkaline phosphate solutions (ie. aqueous Na_3PO_4) would be preceded by formation of HgO . It seems likely that simultaneous formation of Hg_2HPO_4 and $(\text{Hg}_2)_3(\text{PO}_4)_2$ occurs depending on solution pH and electrode polarization. A solubility product (K_{sp}) has not been published for $(\text{Hg}_2)_3(\text{PO}_4)_2$, but it would probably be much smaller than that of Hg_2HPO_4 (10^{-12}). One may examine, for purposes of comparison, the values of the solubility products for lead (Pb^{2+}) complexes¹³⁹: $\text{Pb}_3(\text{PO}_4)_2$ ($K_{\text{sp}} = 10^{-42}$) and PbHPO_4 ($K_{\text{sp}} = 10^{-10}$). The possibility for forming mercurous complexes with HPO_4^{2-} and PO_4^{3-} ions should be appreciably increased when mercury is anodically polarized, due to enhanced dissolution of mercury as Hg_2^{2+} ions at increased positive potentials^{72,77}. Barradas and co-workers⁷² in a recent paper have used this approach to show, especially in the case of dilute NaF solutions, that localized hydrolysis and complexation effects of mercurous ions are the source of much of the inconsistency in interfacial tension results. While HgO is thermodynamically stable in an alkaline medium ($K_{\text{sp}} = 10^{-25}$), the formation of Hg_2HPO_4 and/or $(\text{Hg}_2)_3(\text{PO}_4)_2$ should not be discounted. In fact, the failure to make a reference electrode reversible to PO_4^{3-} ions⁷⁷ is probably due to the co-existence of HPO_4^{2-} , PO_4^{3-} and OH^- ions.

The cause of discrepancies between interfacial tension and doubly-integrated capacitance for Na_3PO_4 solutions may consequently be due to the presence of HgO as well as the mercurous phosphate complexes: Hg_2HPO_4 and $(\text{Hg}_2)_3(\text{PO}_4)_2$. Similarly, the results of Parsons and Zobel²² could be attributed to formation of Hg_2HPO_4 .

The presence of these insoluble substances is responsible for the miniscus-sticking and contact angle problems in the capillary of the Lippmann electrometer.

E. Anion Adsorption at the Uncharged Electrode

From electrocapillary measurements in Na_3PO_4 the interfacial tension maximum (γ^{max}) was found to be relatively constant at $427.6 \pm 0.2 \text{ mNm}^{-1}$ for concentrations in excess of 0.010M (Table V). A linear plot of γ^{max} against $a_{\pm}$ actually had a small slope yielding a value of $-0.06 \text{ } \mu\text{C cm}^{-2}$ for the relative surface excess of salt at the p.z.c. (see equation (11)). For Na_2HPO_4 γ^{max} values were derived from related data of Gouy as described above in Section A. The relative surface excess of salt in this case was $-0.39 \text{ } \mu\text{C cm}^{-2}$. Similar data have been reported for typical non-specifically adsorbed anions^{18,29}: F^- (0.0), SO_4^{2-} (-0.3), OH^- (0) and CO_3^{2-} (-2.1) (units are $\mu\text{C cm}^{-2}$). Parsons and Zobel²² also observed γ^{max} to be constant for not too concentrated solutions of NaH_2PO_4 ($C < 0.5 \text{ mol l}^{-1}$).

Streaming potentials (p.z.c.) for both Na_2HPO_4 and Na_3PO_4 were constant (see Tables IV and V). Corrections for liquid junction potential were not made, and would probably not be valid, due to the large uncertainties involved in calculations using standard theoretical treatments, such as the Henderson equation (see ref. 77). Transport numbers required for such methods are difficult to estimate in the present case, because there was not a common ion between the phosphate solutions and the reference electrode (SCE). However, the small variations in p.z.c. values obtained over a

considerable concentration range suggest that liquid junction potentials were probably no greater than a few millivolts, and such minor errors are not of serious consequences especially when investigating the comparative behavior of related phosphates and citrates for example. The average value of the p.z.c. was -431.0 ± 0.6 mV for Na_2HPO_4 (0.0025M to 0.50M) and -431.0 ± 0.8 mV for Na_3PO_4 ($c > 0.010\text{M}$). By contrast, streaming potentials in NaH_2PO_4 were much more negative in concentrated solutions²², reaching a value of about -520 mV (vs SCE) for a 6M solution.

The constancy of the p.z.c. and γ^{max} for di- and trisodium phosphates indicates that specific ionic adsorption does not seem to take place at the uncharged mercury solution interface. In this respect, HPO_4^{2-} and PO_4^{3-} anions (and H_2PO_4^- in dilute solutions $c < 0.1\text{M}$) exhibit properties similar to sulphate, hydroxide, carbonate and fluoride ions^{18,29}.

It is now of interest to determine the adsorption of phosphate ions on positively charged mercury.

F. Anion Adsorption at Positively Charged Mercury

A direct test can be made to detect specific adsorption by examining the agreement between experimental capacitance data and the capacitance of the diffuse layer^{22,140}. In the absence of specific adsorption the total double layer capacitance, C , can be regarded as a series combination of the capacitance of the inner layer, C^i , and the capacitance of the diffuse layer, C^d , which may be written:

$$\frac{1}{C} = \frac{1}{C^i} + \frac{1}{C^d} \quad (54)$$

The diffuse layer capacitance and charge, q^d , were calculated by the GCS theory for unsymmetrical electrolytes using the formulae published by Grahame²¹. Both q^d and C^d were calculated as functions of the OHP potential, ϕ_2 , using Grahame's equations²¹, and in this way C^d was obtained for different values of the charge on the electrode, making use of the fact that in the absence of specific adsorption $q_m = -q^d$. Only in the case of symmetrical electrolytes^{21,22} can C^d be obtained as an explicit function of q_m . The necessary equations are given here for convenience, but similar equations were previously described in Chapter I, Section E.

$$q^d = \frac{A}{\sqrt{I'}} \left[m e^{-ly} + l e^{my} - (m+1) \right]^{1/2} \quad (55)$$

$$C^d = \left(\frac{AFm}{2RT\sqrt{I'}} \right) \frac{(e^{my} - e^{-ly})}{(m e^{-ly} + l e^{my} - (m+1))^{1/2}} \quad (28)$$

$$(\text{Na}_2\text{HPO}_4 : l = l' = 1, m = 2)$$

$$(\text{Na}_3\text{PO}_4 : l = l' = 1, m = 3)$$

Capacitance data for Na_2HPO_4 and Na_3PO_4 , over the concentration range: 0.005M to 0.50M, are plotted according to equation (54) in figure (22a) and (22b), respectively. Straight lines, of slope equal to unity, have been drawn through the points shown in figure (22a) and (22b) for different values of q_m , as given on the right of each line. It is evident that equation (54) is obeyed only near $q_m = 0$, and therefore specific adsorption is indicated, especially at positive charges.

The relative surface excess of anions at constant q_m was calculated for both Na_2HPO_4 and Na_3PO_4 from the capacitance results

Figure 22. Reciprocal capacitance versus reciprocal diffuse layer capacitance for (a) Na_2HPO_4 and (b) Na_3PO_4 solutions. Lines are drawn with unit slope and electrode charge in $\mu C cm^{-2}$ is indicated on the right.

using equation (14) and the computer program described in Chapter II. Constants, ($\gamma^{\max}$ and $E_{(\text{Na}^+/\text{Na})}^{\text{P.Z.C.}}$), for double-integration of capacitance data were listed in Tables IV and V for Na_2HPO_4 and Na_3PO_4 , respectively. The analysis was carried out for 0.005M to 0.50M solutions of Na_2HPO_4 and 0.0025M to 0.50M solutions of Na_3PO_4 ; that is, eight different concentrations for each salt. In figures (23) and (24) $\Gamma_{-(w)}$ is plotted as a function of q_m for Na_2HPO_4 and Na_3PO_4 , respectively. For comparison, in figure (25) some of the results for NaH_2PO_4 , published by Parsons and Zobel²², have been reproduced. The maximum probable errors in $\Gamma_{-(w)}$ were estimated from the r.m.s. deviations of the Parsons' auxiliary function ξ_+ , using as a guide the study of computer-generated double layer errors published by Fawcett and Kent⁸⁹. These errors are shown in figures (23) and (24) by vertical bars which apply only to the regions indicated.

There were some notable differences in the behaviour of the $\Gamma_{-(w)}$ curves for the three sodium phosphate salts. On positively charged mercury, $\Gamma_{-(w)}$ increased with solute concentration for NaH_2PO_4 ($q_m > 7\mu\text{C cm}^{-2}$) and Na_3PO_4 ($q_m > -3\mu\text{C cm}^{-2}$), but in the case of Na_2HPO_4 $\Gamma_{-(w)}$ was approximately independent of concentration below 0.10M. As shown in figure (23), $\Gamma_{-(w)}$ decreased at higher concentrations of Na_2HPO_4 (0.20M and 0.50M). This type of behavior was also reported³⁹ for solutions of NaClO_4 in excess of 2M. In the present work, similar results were obtained for Na_2SO_4 , indicating very little change in the relative surface excess of sulphate ions with concentration over the interval: 0.20M to 1.00M. Decreasing $\Gamma_{-(w)}$ at higher concentrations has been attributed to the adsorption of water in the inner layer³⁹ by Damaskin and

Figure 23. Anion relative surface excess versus electrode charge for Na_2HPO_4 solutions: (a) 0.020M, (b) 0.040M, (c) 0.050M, (d) 0.10M, (e) 0.20M and (f) 0.50M.

Figure 24. Anion relative surface excess versus electrode charge for Na_3PO_4 solutions: (a) 0.005M, (b) 0.010M, (c) 0.020M, (d) 0.050M, (e) 0.10M, (f) 0.20M and (g) 0.50M.

Figure 25. Anion relative surface excess versus electrode charge for NaH₂PO₄ solutions: (a) 0.50M, (b) 0.20M and (c) 0.10M (from ref. 22).

co-workers, but not many observations of this type of behavior have been reported in the literature.

A second interesting difference in the $\Gamma_{-(w)}$ curves was that for NaH_2PO_4 (figure (25)) and Na_3PO_4 (figure (24)) a point of convergence was observed. The intersections of $\Gamma_{-(w)}$ vs. q_m plots occurred at about $q_m = 6\mu\text{C cm}^{-2}$ for NaH_2PO_4 and at $q_m = -3\mu\text{C cm}^{-2}$ for Na_3PO_4 .

A comparison has been made in figure (26) of the relative magnitude of $\Gamma_{-(w)}$ for 0.1M solutions of NaH_2PO_4 , Na_2HPO_4 , Na_3PO_4 and Na_2SO_4 . The data are plotted against the electrode charge for $q_m > 0$. Results for NaH_2PO_4 were taken from the paper of Parsons and Zobel²². The curve for Na_2SO_4 was obtained by the author from capacitance data which were analyzed using the methods applied to Na_2HPO_4 and Na_3PO_4 described above. It is clear from figure (26) that $\Gamma_{-(w)}$ values are much the same for 0.1M solutions of Na_2SO_4 , Na_2HPO_4 and Na_3PO_4 , but for NaH_2PO_4 the relative surface excess of H_2PO_4^- ions is appreciably greater. An estimate of the relative adsorbability of the various anions depicted in figure (26) can be made by comparing the $\Gamma_{-(w)}$ curves with surface excesses calculated from the GCS theory. The diffuse layer surface excess (Γ_-^d) curves for 1:1, 1:2 and 1:3 electrolytes are shown in figure (26) as broken lines. These were calculated from the GCS theory, assuming that both cations and anions were not specifically adsorbed. When the relative surface excess exceeds that predicted by the GCS theory, the difference is due to specific adsorption of ions. Thus in figure (26) it is evident that very little specific adsorption occurs from 0.1M NaH_2PO_4 , but appreciable anion specific adsorption

Figure 26. Comparison of $\Gamma_{-(w)}$ results for 0.10M solutions of (a) NaH_2PO_4 (from ref.22), (b) Na_2SO_4 , (c) Na_2HPO_4 and (d) Na_3PO_4 . Calculated diffuse layer surface excess curves, Γ_{-}^d , are also shown for the different electrolyte types.

is observed from Na_2SO_4 , Na_2HPO_4 and Na_3PO_4 , and increases as q_m becomes more positive. In more concentrated solution of NaH_2PO_4 ($c > 0.1\text{M}$) however, Parsons and Zobel have shown that the H_2PO_4^- exhibits a marked increase in specific adsorption on positively charged mercury. Finally, it is instructive to notice in figure (26) the relative positions of the diffuse layer surface excess (Γ_-^d) for 1:1, 1:2 and 1:3 electrolytes, because the quantitative determination of specifically adsorbed charge depends on Γ_-^d .

Specifically adsorbed charge for anions, q_-' , was calculated by comparing the total charge due to anions, $q_- = z_- F \Gamma_-^d(w)$, with the diffuse layer charge, q_-^d , (see Chapter I, Section E). In the GCS calculations variations of the dielectric coefficient (ϵ) were accounted for by comparison with results published by Hasted, Ritson and Collie⁶⁰ (see also Chapter II). For solutions of Na_2HPO_4 it was assumed that $d\epsilon/dC = -22 \text{ mol}^{-1} \text{ l}$ ie. equal to the value reported for Na_2SO_4 (ref. 60). It was estimated for Na_3PO_4 that $d\epsilon/dC = -29 \text{ mol}^{-1} \text{ l}$ on the basis that $\delta_{\text{Na}^+} = -8 \text{ mol}^{-1} \text{ l}$ and $\delta_{\text{SO}_4^{2-}} \approx \delta_{\text{PO}_4^{3-}} \approx -7 \text{ mol}^{-1} \text{ l}$

$$\text{(ie.) } \frac{d\epsilon}{dC} = \delta_+ + 3\delta_- \quad \text{(see ref. 60).}$$

The results of calculations for anion specific adsorption are shown in figure (27a) and (27b) for Na_2HPO_4 and Na_3PO_4 , respectively. The specifically adsorbed charge, q_-' , is plotted against electrode charge, q_m , for several concentrations. Very little specific adsorption was found for HPO_4^{2-} , and in fact, for a 0.50M solution of Na_2HPO_4 , q_-' was positive over the entire range of positive q_m (broken curve in figure (27a)). These results may be indicative of

Figure 27. Anion specifically adsorbed charge for (a) Na_2HPO_4 and (b) Na_3PO_4 solutions: Δ 0.050M, $\circ$ 0.10M, $\blacktriangle$ 0.20M, $\bullet$ 0.50M.

the level of error possible in calculations of this type for very concentrated solutions. It is questionable as to why the trend in the results for q'_- is so different in the case of Na_3PO_4 , if indeed these are errors due to imperfections in the GCS theory. On a comparative basis, the results in figure (27) indicate that, at the same values of q_m , the PO_4^{3-} ion is more strongly specifically adsorbed than is the HPO_4^{2-} ion. However the fact that trisodium phosphate solutions are a mixture of OH^- , HPO_4^{2-} and PO_4^{3-} ions (see Table VI and figure (20)) presents some difficulty in applying diffuse layer theory to the double layer results. Therefore, q'_- values are likely overestimated for Na_3PO_4 , because of the differences in q_-^d for 1:1, 1:2 and 1:3 type salts (see figure (26), in which $\Gamma_-^d = q_-^d/z_-F$). Only small positive electrode charges could be attained in Na_2HPO_4 and Na_3PO_4 solutions at the mercury electrode, resulting in relatively small values for the respective $\Gamma_{-(w)}$. The errors involved in q'_- calculations are therefore not negligible, due to the differences in location of the Gibbs dividing surface and the OHP. (This was discussed in Chapter I, Section D.) In view of these uncertainties, it is important to consider the specific role of adsorbed water in the mercury-electrolyte interphase.

G. Adsorbed Water and Specific Adsorption

The surface excess of water may be determined in cases when weak specific adsorption occurs. For example, the comparison of experimentally derived cation (relative) surface excesses, $\Gamma_{+(w)}$, with diffuse layer excesses, Γ_+^d , frequently results in negative

values for the charge due to specifically adsorbed cations, q_+^i . For $q_m < 0$, negative specific adsorption (ie. $q_+^i < 0$) has been attributed to the existence of an ion-free layer between the OHP and the electrode surface^{22,39,40,41}.

In the present work, negative q_+^i data were obtained for Na_3PO_4 and Na_2SO_4 at the negatively charged mercury interface. By rearrangement of equation (5a) the surface excess of water was evaluated, assuming the GCS theory could be used to calculate cation surface excess, $\Gamma_+ \equiv \Gamma_+^d$.

$$\Gamma_w = (\Gamma_+ - \Gamma_{+(w)}) \frac{x_w}{v_+ x_{\text{salt}}} = (\Gamma_+^d - \Gamma_{+(w)}) \frac{x_w}{v_+ x_{\text{salt}}} \quad (56)$$

Results are compared for (0.10M, 0.20M and 1.00M) Na_2SO_4 and (0.10M, 0.20M and 0.50M) Na_3PO_4 and are found in figure (28). The broken horizontal line in figure (28) indicates Γ_w equivalent to a monolayer of adsorbed water. For both Na_3PO_4 and Na_2SO_4 Γ_w was positive over a wide range of q_m (ie. zero to $-17 \mu\text{C cm}^{-2}$) and as q_m became more negative the surface excess of water appeared to slowly increase. However, at constant q_m there was a notable decrease in Γ_w with increasing solute concentration. For solutions of Na_2HPO_4 values of Γ_w were very small for all concentrations investigated and amounted to only plus or minus one-tenth of a monolayer of water (ie. $\pm 1 \times 10^{-10} \text{ mol cm}^{-2}$).

An interpretation of the behavior of Γ_w as seen in figure (28) is complicated by the fact that one does not know the movement of the Gibbs dividing surface relative to the fixed OHP as a function of concentration. The decreasing values calculated for Γ_w (figure (28)) may reflect movement of the Gibbs dividing plane at higher concentrations. However, the nature of individual ionic hydration

Figure 28. Surface excess of water versus electrode charge for Na_2SO_4 ($\square$ $\circ$ $\triangle$) and Na_3PO_4 ($\triangle$ $\bullet$ $\blacksquare$) at different concentrations as indicated.

of the species involved could also have this effect^{39,109}. A decrease in Γ_w has also been reported⁴⁰ for concentrated solutions of LiCl and NaClO₄ ($c > 4 \text{ mol l}^{-1}$). Harrison et al. concluded that a decrease in the thickness of the adsorbed water layer (which may be taken as equivalent to a decrease in Γ_w) corresponded to a larger degree of ionic hydration⁴⁰. Strong interactions between water and ionic components of the diffuse layer could partially deplete the interphase of some of its bound water in order to satisfy hydration requirements of the ions. In contrast to the chloride and perchlorate ions mentioned above, sulphate and phosphate ions are strongly hydrated^{20,117}, so that with the added presence of Na⁺ ions there is probably a very great competition for water molecules in the vicinity of the OHP. The importance of ion-water interactions will be discussed further after dealing with the problem of adsorbed water on positively charged mercury.

For $q_m > 0$, q'_- was found to be zero, and in the particular case of Na₂HPO₄ even positive values were obtained. Results of a similar type were reported for NaH₂PO₄ by Parsons and Zobel²². Positive q'_- (ie. negative specific adsorption of anions) suggests the existence of a layer of adsorbed water on the electrode, analogous to the situation discussed above for cations when $q_m < 0$. Assuming such a possibility for Na₂HPO₄ and Na₃PO₄ adsorption, the surface excess (Γ_- , see equation (5)) was calculated from the experimental relative surface excess ($\Gamma_{-(w)}$) using an empirical model for the surface excess of water. The thickness of the ion-free layer was taken equal to the diameter of a water molecule (2.8Å) and its density as that of normal water at 25° (0.99807 g ml⁻¹). The resulting surface

excess for water was $\Gamma_w = 1.55 \times 10^{-9} \text{ mol cm}^{-2}$. These assumptions are plausible because of the small electrode charges involved.

Therefore equation (5) becomes:

$$\Gamma_- = \Gamma_{-(w)} + \nu_- \left(\frac{x_{\text{salt}}}{x_w} \right) 1.55 \times 10^{-9} \quad (57)$$

In equation (57) $\Gamma_{-(w)}$ is an experimental quantity and (x_-/x_w) is easily calculated from density measurements.

For the H_2PO_4^- ion Parsons and Zobel²² estimated saturation coverage equal to $-53 \mu\text{C cm}^{-2}$ on the basis of hexagonal close packing of spheres, $2.94 \text{ \AA}$ in radius. A similar value should be appropriate for the HPO_4^{2-} and PO_4^{3-} ions. Since $\Gamma_{-(w)}$ never exceeded about $3.5 \times 10^{-11} \text{ g.ion cm}^{-2}$ for either Na_2HPO_4 or Na_3PO_4 at highest positive q_m (see figures (23) and (24)), it is clear that surface coverages by adsorbed HPO_4^{2-} or PO_4^{3-} ions were very small (ie. less than 15%). Therefore the model for an adsorbed layer of water is fairly reasonable and thus permitted a recalculation of anion surface excess by equation (57).

It must be stressed that the use of an empirical model for adsorption of water at the electrode interface does not give thermodynamic validity to the values of Γ_- calculated by equation (57). There is no method of determining Γ_w directly^{16,17}, so one must of necessity attempt to use a model or phenomenological approach which at best is somewhat tenuous, in order to calculate Γ_- . If the model chosen is a reasonable one, its value lies in deriving some knowledge of the relative behavior of adsorbed ions and water in the interphase. It should be emphasized that with nonthermodynamic assumptions inherent in the model the numbers

calculated for Γ_- have no absolute meaning. Previously calculated q_-^I data were corrected to account for electrode bound water. Corrected values of specifically adsorbed charge, q_-^{II} , are given by equation (58).

$$q_-^{II} = (\Gamma_- - \Gamma_-^d) z_- F \quad (58)$$

In equation (58) Γ_-^d was computed from the GCS theory and Γ_- came from use of equation (57) as described above. The difference between the specifically adsorbed charge, q_-^I (see Section F), and its corrected value, q_-^{II} , is simply:

$$q_-^{II} = q_-^I + z_- F \left(\frac{x_-}{x_w} \right) \times 1.55 \times 10^{-9} \quad (x_- = v_- x_{\text{salt}}) \quad (59)$$

The last term in equation (59) became appreciable for 0.50M Na_3PO_4 ($-4.02 \mu\text{C cm}^{-2}$) and for 0.50M Na_2HPO_4 ($-2.72 \mu\text{C cm}^{-2}$). In their paper on NaH_2PO_4 Parsons and Zobel²² reported anion specific adsorption, corrected for water adsorbed in the inner layer as has been done for the present work on Na_2HPO_4 and Na_3PO_4 .

In figure (29) q_-^{II} has been plotted as a function of q_m for Na_3PO_4 (0.50M to 0.05M), Na_2HPO_4 (0.20M to 0.05M) and 0.50M NaH_2PO_4 . Only three points could be shown for 0.50M NaH_2PO_4 in figure (29) because no data were reported²² for $q_m < 6 \mu\text{C cm}^{-2}$. It was deduced from inspection of figure (29) that the relative order of specific adsorption was: $\text{Na}_3\text{PO}_4 > \text{NaH}_2\text{PO}_4 > \text{Na}_2\text{HPO}_4$.

The degree to which the different phosphate ions are specifically adsorbed at mercury may be related to the nature of ion-water interactions as mentioned previously. Indirect supporting evidence for such an effect was obtained from the viscosity B coefficients which are listed here for the three ions of interest.

Figure 29. "Corrected" anion specifically adsorbed charge for: $\square$ (NaH_2PO_4 , ref.22), $\circ$ (Na_2HPO_4) and $\bullet$ (Na_3PO_4). Concentrations: a(0.050M), b(0.10M), c(0.20M) and d(0.50M).

<u>Ion</u>	<u>Viscosity B-Coefficient for the Anion</u>
H_2PO_4^-	0.31
HPO_4^{2-}	0.48
PO_4^{3-}	0.619

As noted before, ions which promote increased order in the structure of water have positive B-coefficients and these may be used as an estimate of ion-solvent interaction. Due to the similarity of shape and size of the phosphate ions their B-coefficients provide a quantitative indication of the relative importance of increasing electrostatic forces on going from the triply-charged PO_4^{3-} ion to the univalent H_2PO_4^- ion. The H_2PO_4^- ion with the smallest B-coefficient was specifically adsorbed to a greater extent than the more structure ordering ion, HPO_4^{2-} . The position of Na_3PO_4 in the sequence of specific adsorption as given above may be anomalous. The amount of specifically adsorbed charge calculated for Na_3PO_4 is probably due to the predominant adsorption of hydroxyl-ions. As mentioned earlier, the mixture of ions present in trisodium phosphate makes it very difficult to apply the GCS theory. The PO_4^{3-} ions themselves are probably not specifically adsorbed to any great degree because of the very strong interaction with water as indicated by the large B-coefficient. It has been mentioned by other workers^{39,135} that strong ion-water interactions result in a very close, quasi-lattice structure in the diffuse part of the double layer. Such effects could be the cause of the peculiar concentration dependence of $\Gamma_{-(w)}$ observed for Na_2HPO_4 and Na_2SO_4 in the present work and for NaClO_4 as reported by Damaskin and colleagues³⁹.

While comparative discussion on varying degrees of ion-free layers is the accepted practice in the literature^{22,39,40,41,108}, it may be somewhat of an artefact for highly hydrated ions such as the phosphates^{20,117}. The calculation of Γ_w in the manner described in the literature and in this thesis does not take into account the fact that the field of the electrode is approximately of the same order of magnitude as the local field of the anions in the interphase. It is difficult to accept that the electrodic field could entirely strip such highly hydrated ions as SO_4^{2-} , H_2PO_4^- , HPO_4^{2-} or PO_4^{3-} of one or more of their waters of hydration at the interface. These oxy-anions exhibit specific adsorption as demonstrated above, but not so extensively or to the same degree of "contact ion adsorption" as in the cases of highly polarizable Br^- and I^- . For HPO_4^{2-} and PO_4^{3-} ions the nature of specific adsorption is very closely connected with strong ion-water interactions. These effects may be so large as to create near the OHP a quasi-lattice structure formed by phosphate anions which are hydrogen bonded to neighbouring water molecules. Such a framework could act as a barrier to further anion adsorption as indicated by the constancy of $\Gamma_{-(w)}$ in Na_2HPO_4 and Na_2SO_4 solutions. A further property of this quasi-lattice structure is demonstrated by the absence of a capacitance hump in Na_2HPO_4 and Na_3PO_4 solutions. Structural order in the interphase may be so high that ions at the OHP do not allow water molecules adsorbed in the inner layer any freedom to reorient in the electrodic field -- consequently a capacitance hump does not occur. It is possible that the capacitance rises very rapidly on positively charged mercury due to a localized pH increase near the

interface¹¹². This could result from strong competition between the electrode and diffuse layer phosphate ions for electrode-bound water. As q_m increases the O-H bond of the adsorbed water dipole is ruptured, resulting in formation of OH^- on the surface. This is shown in figure (30) which illustrates a simplified and speculative model for the formation of a quasi-lattice structure in phosphate solutions in the diffuse layer.

It is not possible with the present results to make an unequivocal assessment of anion specific adsorption of Na_2HPO_4 and Na_3PO_4 at the mercury electrode, because of the limited extent to which the metal can be anodically polarized. As reported for the Hg/NaOH interface²⁶, this is a rather unfortunate characteristic for it only allows analysis of components of charge to be made in the region of small q_m where the accuracy of calculations is somewhat limited.

In conclusion it is important to note that the relatively small amount of specific adsorption observed in solutions of Na_2HPO_4 is an important property from the point of electrochemical adsorption. Studies of the adsorption of organic ions and molecules can be made in aqueous solutions of Na_2HPO_4 as a supporting electrolyte without significant interference from competitive adsorption of its ions.

Figure 30. Schematic diagram for adsorbed PO_4^{3-} at a mercury electrode.

CHAPTER VIDOUBLE LAYER STUDY OF
CITRATE SOLUTIONSA. Introductory Remarks

In the previous chapter attention was focused on characterizing the adsorption at a mercury electrode of Na_2HPO_4 and Na_3PO_4 and making comparisons with published results for NaH_2PO_4 (ref. 22). It was established that phosphate anions are specifically adsorbed only on positively charged mercury and that anodic polarization for Na_2HPO_4 and Na_3PO_4 is very limited compared to the extent of positive charging reported for mono-sodium dihydrogen phosphate. The steep anodic rise of capacitance curves for Na_2HPO_4 and Na_3PO_4 was tentatively interpreted by a modelistic approach, involving strong structural interactions involving electrode bound water.

The double layer work presented here is an extension of the previous study on phosphates in that it considers the electrochemical adsorption of much larger oxy-anions. Of specific interest in this study of citrate salts is the reported⁵⁴ ion-pairing which occurs in the bulk solution. Citrates and phosphates are related in respect to the interests of the present work by virtue of the fact that both series of anions are very effective water structure-ordering entities. This property and others will be shown to play a very important role and allows the Jenard and Hurwitz theory⁶² to be applied successfully to the results.

In this chapter, results will be given for double layer studies of aqueous solutions of different sodium salts of citric acid at the ideally polarized mercury electrode. To introduce some of the important aspects of these investigations, the discussion will first

be centered around considerations of solution pH and the ionic composition of citrate electrolytic solutions. A résumé of evidence concerning ionic association in the homogeneous solution phase will also be presented. This is followed by a discussion of some solution structural properties, as determined by viscosity and density studies, as well as other related information.

The main body of experimental data was obtained in disodium and trisodium citrate solutions at 25°C. These primary double layer data (ie. interfacial tension and capacitance) were treated by thermodynamic methods to obtain derived data as outlined in the first chapter.

The emphasis has been to perform thermodynamic analysis for adsorption at a positively charged electrode and to interpret the findings in terms of the homogeneous properties of the respective salt solutions. Throughout these studies the reliability of double layer measurements was ascertained by using the criterion that a reasonable agreement is found for the directly measured interfacial tension and that obtained by doubly integrating capacitance results.

B. Homogeneous Properties of Citrate Salt Solutions

1. pH Dependence of Ionic Species

It is important to establish the identity of ionic species present in aqueous sodium citrate solutions as a precursor to any attempts at describing the nature of adions in the electrical double layer. Citric acid is a tribasic carboxylic acid whose structural formula is:

Since the carboxyl groups are well separated in the acid molecule, the successive ionization constants at 25° are rather close together in value⁹⁰: $\text{p}K_1 = 3.14$, $\text{p}K_2 = 4.78$ and $\text{p}K_3 = 6.38$. Consequently, over a considerable pH range at least two anionic species will co-exist in citrate solutions. Figure (31) demonstrates the varying composition of citrate species as a function of pH in homogeneous solution. The curves were plotted for a concentration of 0.10M using the following expressions derived from consideration of the various equilibria involved in aqueous solutions⁸⁶:

$$\alpha_3 = \frac{[\text{H}_3\text{Cit}]}{C} = \left[1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1 K_2}{[\text{H}^+]^2} + \frac{K_1 K_2 K_3}{[\text{H}^+]^3} \right]^{-1} \quad (60)$$

$$\alpha_2 = \frac{[\text{H}_2\text{Cit}^-]}{C} = \alpha_3 \frac{K_1}{[\text{H}^+]} \quad (61)$$

$$\alpha_1 = \frac{[\text{HCit}^{2-}]}{C} = \alpha_3 \frac{K_1 K_2}{[\text{H}^+]^2} \quad (62)$$

$$\alpha_0 = \frac{[\text{Cit}^{3-}]}{C} = \alpha_3 \frac{K_1 K_2 K_3}{[\text{H}^+]^3} \quad (63)$$

In the above, α_3 is the fraction of total citrate present as the undissociated acid, H_3Cit ; the other fractions ($\alpha_0, \alpha_1, \alpha_2$) are defined by equations (61) - (63). It follows that

$$\alpha_0 + \alpha_1 + \alpha_2 + \alpha_3 = 1 \quad (64)$$

Figure 31. Theoretically calculated percentage of various species present in 0.10M citrate solution versus pH; (O) refer to composition of $NaCit^{2-}$, (X) corresponding amounts of Cit^{3-} (according to ref.54).

The total concentration of citrate is C , in moles per litre of solution. It is evident from inspection of figure (31) that salt solutions in which only a single anionic species exists must have $\text{pH} > 8$. For example, 0.1M disodium hydrogen citrate solution has the following approximate composition: 75.3% HCit^{2-} , 15.6% Cit^{3-} and 9.1% H_2Cit^- . The calculations (graphically illustrated in figure (31)) used ionization constants of citric acid, extrapolated to zero ionic strength as reported by Bates and Pinching⁹⁰. The curves of figure (31) are therefore not exact and may vary somewhat with concentration, but nevertheless they represent a fairly good description of the simultaneous equilibria present in solutions which are of interest in the present work.

2. Ion-Association in Citrate Solutions

In addition to the ionic equilibria just described, it is apparent that alkali metal cations associate with Cit^{3-} and perhaps with HCit^{2-} anions as well. From measurements done with a sodium ion responsive electrode in 0.1M Na_3Cit solution, formation constants of 5.0 ($\text{pH} = 8.3$) and 4.2 ($\text{pH} = 8.0$) were reported⁵⁴ for a complex ion, NaCit^{2-} :

In view of the apparent pH dependence of K_f , measurements of Na^+ activity were made to confirm the presence of such a species. A sodium ion responsive electrode was first calibrated with standard NaCl

solutions. The activity of cations present in citrate solutions was then determined by e.m.f. measurements, assuming negligible differences in activity coefficients between dilute (less than 0.1M) chloride and citrate solutions. Results of these experiments are shown in figure (32) for citrate solutions at different pH values. The broken curve represents the number of Na^+ ions per citrate species (n) which should theoretically be present based on the reported ionization constants for citric acid. Points on the experimental data for 0.005M solution which clearly indicate a decrease in n at $\text{pH} > 7$. In fact, n approached a constant value equal to 2 at $\text{pH} = 9$; this particular feature was found to be independent of concentration. For 0.001M solutions the maximum at $\text{pH} = 7$ was $n \approx 3$, and in more concentrated solutions ($C > 0.2\text{M}$) this peak decreased to $n = 2$.

The decreased activity of Na^+ corroborates the findings of previous workers⁵⁴, however the "complex" is certainly very weak. The attraction between Na^+ and Cit^{3-} is electrostatic rather than covalent and therefore the associated particle is called an ion-pair according to a definition proposed by Nancollas⁹¹. This is substantiated by plotting $\log K_f$ against a coulombic energy term⁹² ($z_+z_-/(r_+ + r_-)$, where z_+ and z_- are the cation and Cit^{3-} ionic charges, respectively, and r_+ and r_- the ionic radii (Pauling's⁹⁷ values for the alkali cations). The data are plotted in figure (33). On the basis of measurement of a Courtauld molecular model and density results to be discussed below, the radius of the Cit^{3-} ion was $r_- = 3.5 \text{ \AA}$. Formation constants, K_f , were taken from a paper by Rechnitz and Zamochnick⁵⁴. The plot shown in figure (33) has

Figure 32. Plot of the number of sodium ions per citrate anion as a function of pH. (O) experimental points, (---) theoretical values, solution concentration 0.005M.

Figure 33. Ion-pair formation constant versus coulombic energy term for alkali metal citrates.

two linear portions and indicates that K_f decreases from Li^+ to Cs^+ . According to Davies⁹², the results of figure (33) are a good indication of the importance of electrostatic interionic forces.

Other associated species may also be present in citrate solutions, especially at higher concentrations where the dielectric coefficient is reduced in value and the activity coefficient of water may depart significantly from unity. There is some evidence⁵⁵ that NaHCit^- exists between $\text{pH} = 5$ and $\text{pH} = 6$, but Na^+ activity measurements did not detect this entity in dilute solutions.

3. Size of Cit^{3-} Ion

Standard formulae⁹⁴ were used to calculate apparent molal volume, ϕ_v , and partial molal volume, $\bar{V}$, from density data obtained for the alkali metal citrate solutions (see Chapter IV, Section C). Equation (66) was applied to density results to calculate ϕ_v :

$$\phi_v = \frac{1000}{c} - \frac{1}{D_0} \left[\frac{1000D}{c} - M \right] \quad (66)$$

and $\bar{V}$ was obtained using equation (67).

$$\bar{V} = \frac{M - 1000 \left(\frac{dD}{dc} \right)}{D - c \left(\frac{dD}{dc} \right)} \quad (67)$$

The formula weight of the anhydrous salt is M and the concentration dependence of solution density, D , was evaluated by differentiation of equation (52).

$$\frac{dD}{dc} = k_2^2 + k_1 k_2 c^{-1/2} \quad (68)$$

Results of these calculations gave ϕ_v and $\bar{V}$ values which could not

be extrapolated to infinite dilution with much certainty. This can be seen in figure (34) where ϕ_v and $\bar{V}$ are plotted against $\sqrt{c}$ for Li_3Cit solutions. Results having trends similar to those in figure (34) were obtained for Na_3Cit and K_3Cit solutions. For most electrolytes the functional dependence of partial molal volume on solute concentration is of the Debye-Huckel type^{81b}, as given by equation (69),

$$\bar{V} = \bar{V}^0 + S c^{1/2} \quad (69)$$

in which S is a constant and the partial molal volume at infinite dilution, $\bar{V}^0$, is equal to the apparent molal volume at infinite dilution, ϕ_v^0 . The results in figure (34) show that ϕ_v and $\bar{V}$ both decrease upon dilution, but are not in adequate agreement with equation (69) to permit extrapolation to zero concentration. It may be that for such highly unsymmetrical electrolytes (ie. the alkali metal citrates) the Debye-Huckel approximation is not valid for $c > 0.01\text{M}$. Average values of $\bar{V}$ were calculated over the concentration range: 0.02M to 0.10M . These are listed in Table VIII along with the limiting apparent molal volumes of the alkali cations⁵⁸, ϕ_{v+}^0 . The partial molal volume of the Cit^{3-} ion, $\bar{V}_-$, was estimated thus:

$$\bar{V}_- = \bar{V} - 3\phi_{v+}^0 \quad (70)$$

Use of equation (70) necessarily diminishes solvent electrostrictive effects by attributing them mostly to the cation⁵⁸. All three salts listed in Table VIII thus gave approximately equal values for $\bar{V}_-$. Therefore the average partial molal volume of the Cit^{3-} ion may be taken as 96.3 ml mol^{-1} , with a certain amount of reliability. The effective radius of the anion, r_e , can then be calculated, assuming

Figure 34. Apparent molal volume (ϕ_v) and partial molal volume ($\bar{V}$) results for aqueous solutions of $\text{Li}_3\text{Cit.}$ at 25.0°C.

TABLE VIII Partial Molal Volume Results at 25°

	Average $\bar{V}$	ϕ_{v+}^0	$\bar{V}_-$	r_e
	(0.02M < C < 0.10M) (ml mol ⁻¹)	(ref. 58) (ml mol ⁻¹)	(eqn. 70) (ml mol ⁻¹)	(eqn. 71) (Å ³)
Li ₃ Cit	75.8	-6.6	95.6	3.36
Na ₃ Cit	76.6	-7.0	97.6	3.38
K ₃ Cit	105.7	3.3	95.8	3.36
Citric Acid	113.0 (ref. 93)			
Averages: $\bar{V}_- = 96.3 \text{ ml mol}^{-1}$, $r_e = 3.37 \text{ Å}^3$				

a spherical particle:

$$r_e^3 = \frac{3}{4\pi N} (\bar{V}_-) \quad (71)$$

where N is Avogadro's number. Values of r_e obtained using equation (71) agree quite well with the dimensions of a Courtauld molecular model of citric acid (ie. approximately $3.5 \text{ \AA}^0$). These results are also reported in Table VIII (column five).

With the Bjerrum theory^{95,96} for ion association, some calculations were made for the alkali metal citrate salts, using formation constants published by Rechmitz and Zamochnick⁵⁴. The distance of closest approach, a , was determined and Pauling⁹⁷ radii (r_+) were used for the cations to estimate the interionic distance in the ion-pair, x .

$$x = a - (r_+ + r_e) \quad (72)$$

The average effective radius for Cit^{3-} was taken as $3.37 \text{ \AA}^0$. The results are given in the following tabulation:

Electrolyte	K_f	a	r_+	x
	(1/mol)	(Angstrom Units ($\text{\AA}^0$))		
Li_3Cit	6.8	9.65	0.60	5.68
Na_3Cit	5.0	9.96	0.95	5.64
K_3Cit	3.9	10.1	1.33	5.4
Rb_3Cit	3.1	10.2	1.48	5.3^5
Cs_3Cit	2.1	10.3	1.69	5.2
Reference	(54)	(96)	(97)	

Although these are simplified calculations they do indicate that an ion-pair formed between an alkali metal cation and a Cit^{3-} anion probably is separated by two water molecules. Taking the diameter of a water molecule as $2.78 \text{ \AA}$, gives a distance of $5.56 \text{ \AA}$ between ions in the pair; in reasonable compatibility with the values of x listed above. Ion pairs formed by Cit^{3-} and an alkali metal cation are therefore probably of the "hydration shell contact type" illustrated in figure (5c).

4. Structure-Ordering by Citrate Ions

The results of viscosity measurements in citrate salt solutions, over a wide pH range, provide good qualitative evidence that structure-ordering takes place. The value of the viscosity B-coefficient, calculated for the species, Cit^{3-} , depended on the counter-ion and therefore was affected by ion-pairing (see Table I). Davies and Malpass⁹⁸ showed that allowance could be made for ion association by introducing into the Jones-Dole equation a correction for the degree of electrolyte dissociation. This type of analysis was done for the lithium, sodium and potassium citrate viscosity data, using Rechnitz and Zamochnick's formation constants⁵⁴. The results of these calculations were mainly inconclusive, since agreement with the corrected form of the Jones-Dole equation could not be obtained. However, an approximate value was deduced for the viscosity B-coefficient for Cit^{3-} , $B \approx 0.72$. By plotting the formation constant K_f , against the B-coefficient (as calculated without regard for ion-pairing; listed in Table I) another value was obtained for the B-coefficient, in the limit where $K_f \rightarrow 0$, which roughly corresponds to

the unpaired Cit^{3-} ion: $B \approx 0.67$. With reasonable certainty it may therefore be assumed that the viscosity B-coefficient for the Cit^{3-} anion is: $B \approx 0.70 \pm 0.03$. Such a large and positive B-coefficient indicates a high degree of structure ordering in solution. From the values estimated for the ionic B-coefficients for HCit^{2-} and H_2Cit^- (see Table II), these ions appear to have a somewhat smaller effect on the solution structure. In general, it is probably the large size of the citrate species, coupled with a great affinity to form hydrogen bonds with water, that account for the large, positive B-coefficients⁴⁴. The value obtained for the activation energy of viscous flow for the Cit^{3-} ion $\Delta E_{\ddagger}$ was about $+100 \text{ cal mol}^{-1}$. The errors involved in this calculation are about $\pm 200 \text{ cal mol}^{-1}$, so $\Delta E_{\ddagger}$ could be in the range $+300$ to $-100 \text{ cal mol}^{-1}$. It is not likely that Cit^{3-} could be placed in class IV of Nightingale's classification⁴³, since the type of hydration is most likely similar to that of the class II ions. It would be expected that the $-\text{COO}^-$ groups interact strongly with only one layer of solvent, because the electrical field for such a large ion decreases rapidly with distance. Bonding between carboxylate groups and solvent is probably also directionally oriented due to the localization of charge in the $-\text{COO}^-$ group and the spatial orientation of these groups at the ion surface. It is the author's opinion, therefore that Cit^{3-} be considered as a class II structure-ordering ion in Nightingale's scheme. The phosphate ions may also be considered members of this class, because of their comparably large, positive B-coefficients.

The agreement of experimental and calculated viscosity A-

coefficients is quite good. They decrease, as expected, in the same order as the tendency towards ion-pair formation diminishes. It should be noted that for Na_3Cit , $A \approx 0.04$, is considered a numerically significant value in comparison, say for example, with MgSO_4 ($A = 0.023$)⁴⁴.

In figure (35) the ionic B-coefficients have been plotted against ionic partial molal volumes ($\bar{V}_\pm$) to show the effect of size of structure-ordering carboxylic acid anions on the viscosity of aqueous solutions. The data were collected from various sources (eg. 44,74,98,99) and in some cases only approximate values of the B-coefficients could be obtained. This was done by assuming linear Jones-Dole behavior up to 0.1M and neglecting the A-coefficient for the following: Na n-butyrate, Na-formate, K_2 -oxalate. A straight line seems to fit the data points for the highest valency of the polybasic anions. In any one ionic system containing two or more species (eg. citrates, maleates and fumarates), a straight line appears to roughly fit the data. This is shown by broken line segments in figure (35). The structure-ordering of water by these anions therefore increases with ionic size and ionic charge. The isomeric maleate and fumarate ions have almost identical B-coefficients. The hydrophobic alkyl group of the n-butyrate anion possibly accounts for a smaller viscosity effect in this case. The citrate anion seems to fit quite well into the overall scheme of these types of anions.

C. Preliminary Double Layer Measurements

Some double layer experiments of an exploratory nature were

Figure 35. Viscosity B-coefficient versus partial molal volume for some carboxyl anions.

conducted using a variety of solution conditions so that an assessment could be made of the type of ionic adsorption to be expected from the citric acid-citrate salt system. Since electrocapillary measurements are time consuming and tedious, only the faster differential capacitance method was used in this work.

In the first study, capacitance curves were recorded for constant ionic strength (0.60M) combinations of Na_2SO_4 and trisodium citrate (Na_3Cit). These are shown in figure (36) as a set of seven curves; the p.z.c. is given for each relative to the SCE potential scale. As indicated by comparing curves A and B, only a small proportion of citrate salt produced a significant change on the capacitance. Increasing the citrate to sulphate ratio caused the capacitance hump to move towards more negative potentials and to smaller values of capacitance. With increased citrate, the p.z.c. was shifted negatively, indicative of a greater amount of anion specific adsorption.

Although relative surface excesses can be derived from data for 1:1 electrolyte mixtures (eg. KI + KF, ref. 100) the sulphate-citrate system is a much too complicated case for carrying out the usual type of equilibrium double layer calculations. This is due first to uncertainty regarding assignment of activity coefficients for combinations of unsymmetrical salts, and secondly there is the probability that both types of anion are simultaneously specifically adsorbed and it is difficult to isolate their individual contributions to the relative surface excess.

In another series of experiments, capacitance curves were measured for 0.10M Na_3Cit in two different supporting electrolytes:

Figure 36. Anodic part of capacitance curves for constant ionic strength mixtures: $x(\text{mol l}^{-1})\text{Na}_2\text{SO}_4 + (0.1 - 0.5x)(\text{mol l}^{-1})\text{Na}_3\text{Cit}$. $x =$, 0.20(a), 0.19(b), 0.18(c), 0.14(d), 0.10(e), 0.02(f) and 0.0(g).

(1) KCl, and (2) NaClO₄, at the same ionic strength as the sulphate-citrate system. From these results it was found that only in the case of sulphate was the added citrate anion effective in changing the shape of the capacitance curve of the supporting electrolyte. On a comparative basis, it would appear from these experiments that the citrate ion is more strongly specifically adsorbed than sulphate, but less than either perchlorate or chloride ions.

With 0.10M Na₂SO₄ as supporting electrolyte, capacitance curves were recorded for 0.05M citrate solutions of differing pH:

Na₃Cit, pH = 8.2

Na₂HCit (disodium hydrogen citrate), pH = 5.6

NaH₂Cit (sodium dihydrogen citrate), pH = 3.9

H₃Cit (citric acid), pH = 2.6

The data are shown in figure (37) for pure 0.10M Na₂SO₄ and the four salt mixtures. A reversible curve could not be obtained for the citric acid at potentials more negative than approximately -0.6 volts.

Capacitance was also measured for pure 0.10M citrate solutions at varying pH, going from the extreme: Na₃Cit to citric acid. The curves are shown in figure (38). Again, at most negative potentials reversible capacitance data could not be obtained for pH = 3.48 and pH = 2.66.

Several facts were established from the studies described above. The first important feature was that capacitance curves for higher pH citrate salts resembled those of inorganic salts such as Na₂SO₄ and the carboxylic acid salts studied by Miller and Grahame³⁰ (eg. sodium salts of oxalic, adipic, glutaric and 1,2,3-propane-

Figure 37. Capacitance curves for 0.10M Na_2SO_4 with 0.05M citrate added. Curve a(supporting electrolyte, pH = 6.6, pure 0.10M Na_2SO_4), b(pH = 8.2), c(pH = 5.6), d(pH = 3.9) and e(pH = 2.6).

Figure 38. Capacitance curves for 0.10M sodium--citrate solutions of different pH. The p.z.c. is shown by a short vertical line for some of the curves.

tricarboxylic acids). This contrasts the type of behavior exhibited by some other organic salts, such as sodium benzene *m*-disulphonate¹⁰¹, which have large capacitance features (eg. pronounced humps) unlike many inorganic salts. The capacitance hump in figure (38), which was observed in solutions of higher pH ($5 < \text{pH} < 9$), gradually disappeared as the pH decreased to acidic values. This may result from the greater adsorptivity of the H_2Cit^- ion or the undissociated acid molecule. It is now well known from studies of organic bases that the electrocapillary curve is depressed more by the undissociated molecule than by its conjugate ion due to stronger adsorption of the non-ionic component¹¹⁰⁻¹¹⁶. The non-reversibility of capacitance curves at lower pH also suggested that non-equilibrium adsorption was probably due to the presence of the acid molecule or singly charged anion. The decrease in capacitance seen in figure (38) near the p.z.c., as pH decreased, was an additional factor indicating that specific adsorption of citrate species probably increases in the order: $\text{Cit}^{3-} < \text{HCit}^{2-} < \text{H}_2\text{Cit}^- < \text{H}_3\text{Cit}$.

These preliminary experiments served to guide future detailed investigations, since pH is a very important variable which had to be controlled in order to obtain meaningful results. It was also recognized that reliable data would not be accessible for NaH_2Cit due to the presence of a significant amount of undissociated (and highly adsorbable) citric acid in such solutions.

It was decided to attempt a complete experimental investigation of the disodium and trisodium salts, in which more dependable data were likely to be acquired. At least in the case of Na_3Cit the identity of the anionic species was fairly well understood (see Sections B.1 and B.2).

D. Disodium Citrate

Capacitance and interfacial tension measurements were made for two independent studies of disodium citrate solutions. For the first study, solutions were prepared by dissolving appropriate amounts of salt ($\text{Na}_2\text{HCit} \cdot 1.5 \text{ H}_2\text{O}$) in triply distilled water. The pH at each different concentration was measured and is listed in Table IX. This will be referred to as the "variable pH" study.

Solutions for the second study of Na_2HCit were adjusted to $\text{pH} = 5.50 \pm 0.03$ by addition of NaOH . This pH value (5.50) was chosen because it is mid-way between pK_2 and pK_3 for citric acid. This is shown in figure (31) as the maximum of the curve labelled " HCit^{2-} ". References will be made in this case to the "constant pH" study.

Some of the results for Na_2HCit are given in Tables IX and X for the variable pH and constant pH studies, respectively. Capacitance curves are shown in figures (39) and (40) for the variable pH and constant pH work, respectively. For the latter a reversible capacitance curve could not be obtained only in the case of 1.00M solution, but electrocapillary data were measured for all concentrations investigated.

The capacitance curves in figures (39) and (40) are distinctly different for the two studies, especially in the region of the capacitance hump. For variable pH solutions the hump was quite pronounced and it decreased in height and broadened as the concentration increased. The hump had a different shape for solutions at constant pH (figure (40)) appearing more like an inflection or shoulder on the capacitance curves. For these solutions the

TABLE IX Double Layer Parameters For Na_2HCit - Variable pH Study
at 25°C

conc.	$-E_{\text{P.Z.C.}}^{\text{D}}$ (SCE)	$-E_{\text{P.Z.C.}}^{\text{D}}$ (Na^+/Na)	$C_{\text{P.Z.C.}}^{\text{D}}$	γ^{max}	pH
(mol l^{-1})	(mV.)	(mV.)	($\mu\text{F cm}^{-2}$)	(mNm^{-1})	
0.005	453.0	446	20.3	424.91	5.36
0.010	456.9	460	22.7	425.36	5.28
0.020	461.7	478	25.4	425.39	5.23
0.050	469.8	509	27.2	425.12	5.08
0.10	477.7	532	27.4	424.14	4.97
0.20	489.2	559	26.8	423.60	4.86
0.50	510.0	598	23.7	419.97	4.69
1.00	514.5	626	20.6	415.59	4.63

TABLE X Double Layer Parameters For Na_2HCit - Constant pH Study at 25°C

conc.	$-E^{\text{p.z.c.}}_{(\text{SCE})}$	$-E^{\text{p.z.c.}}_{(\text{Na}^+/\text{Na})}$	$C^{\text{p.z.c.}}$	γ^{max}	pH
(mol l ⁻¹)	(mV.)	(mV.)	($\mu\text{F cm}^{-2}$)	(mNm ⁻¹)	
0.005	450.2	441	20.9	427.06	5.52
0.010	453.6	460	23.2	426.57	5.51
0.020	455.3	479	26.1	426.13	5.48
0.050	461.0	506	27.7	426.44	5.53
0.10	467.5	528	28.4	425.68	5.51
0.20	475.2	550	26.8	425.59	5.48
0.50	491.1	588	25.5	424.65	5.49
1.00*	---	---	----	422.19	5.57

* Capacitance results were not reliable

Figure 39. Capacitance curves for $\text{Na}_2\text{HCit.}$ solutions ("variable pH study"): (a) 0.005M, (b) 0.010M, (c) 0.020M, (d) 0.050M, (e) 0.10M, (f) 0.20M, (g) 0.50M and (h) 1.00M. pH values are listed in Table IX.

Figure 40. Capacitance curves for $\text{Na}_2\text{HCit.}$ solutions ("constant pH study"): (a) 0.005M, (b) 0.010M, (c) 0.020M, (d) 0.050M, (e) 0.10M, (f) 0.20M and (g) 0.50M.

decrease in hump capacitance with increased concentration was not as great as in the case of the variable pH study. In both the variable and constant pH solutions $\gamma^{\max}$ and the p.z.c. changed in the same manner with concentration, but a somewhat greater lowering of $\gamma^{\max}$ was observed for the solutions whose pH was allowed to vary with concentration. Anion specific adsorption at the p.z.c. was detected by the trend in p.z.c. values towards more negative potentials (on SCE scale) as concentration increased, and also by the decrease in $\gamma^{\max}$ (see Tables IX and X). These effects were slightly more pronounced in the study done in solutions of varying pH and it may therefore be inferred that more specific adsorption occurred from these solutions than from the Na_2HCit solutions having pH = 5.5.

Agreement between twice-integrated capacitance (γ_c) and measured interfacial tension (γ_m) was good for the results obtained in the variable pH study, except for 0.005M at extreme positive polarization. As discussed in Chapter IV discrepancies of this type are expected for very dilute solutions. However, in the set of solutions of pH = 5.5 differences between γ_c and γ_m were noted at both highly positive and highly negative potentials for all solutions except those between 0.02M and 0.10M. Direct interfacial tension measurements were probably more susceptible to error for the very dilute solutions, while capacitance data were more prone to experimental error in the most concentrated solutions. The latter situation was detected by the non-reversibility of the capacitance curve for 1.00M Na_2HCit (constant pH study). This may be due to an irreversible adsorption process which becomes

significant only in very concentrated solutions where multiple association of ionic species is a more likely occurrence.

The double layer results for both studies of Na_2HCit were analyzed by calculating the relative surface excess of anions as a function of electrode charge. Activity coefficients for Na_2HAsO_4 , reported by Harned and Owen^{81c}, were used in the absence of data for Na_2HCit . Very good agreement was observed for $\Gamma_{-(w)}$ in the variable pH study when comparison was made of calculations derived from capacitance data and electrocapillary results. This was expected in view of the small differences between γ_c and γ_m . For the constant pH study only the electrocapillary results were used to calculate $\Gamma_{-(w)}$. The GCS calculations for diffuse layer charge were made for a 1:2 electrolyte as described in Chapter I, Section E, and the charge due to specifically adsorbed HCit^{2-} anion, q'_- , was evaluated. Curves of q'_- for both disodium citrate studies are plotted versus q_m in figures (41) and (42).

The validity of the calculation of q'_- is open to some question in the present systems, since disodium citrate solutions are a mixture of two or more anions of dissimilar valency. The most abundant component in homogeneous solutions of disodium citrate is the anion, HCit^{2-} , comprising about 75% of all anions present. However, the results of figures (41) and (42) are primarily only of qualitative interest, and are useful for comparative purposes with corresponding data for trisodium citrate.

In figures (41) and (42) the larger amount of anion specific adsorption for the variable pH study of Na_2HCit can be explained in terms of the composition of these solutions, contrasted with the composition of solutions in the constant pH study. Solutions

Figure 41. Anion specifically adsorbed charge versus electrode charge for Na_2HCit . ("variable pH study"): (a) 0.05M, (b) 0.10M, (c) 0.20M, (d) 0.50M and (e) 1.00M.

Figure 42. Anion specifically adsorbed charge versus electrode charge for Na_2HCit . ("constant pH study"): (a) 0.05M, (b) 0.10M, (c) 0.20M, (d) 0.50M and (e) 1.00M.

of pH = 5.50 actually contain more HCit^{2-} anion than those with pH < 5.5 (ie. solutions in the variable pH work; see Table IX) and equal overall salt concentration. Furthermore, the solutions with varying pH have a larger proportion of the singly-charged anion, H_2Cit^- , than is present in solutions with pH = 5.5. As mentioned above in discussing figure (38) (see Section C), the monovalent citrate anion (H_2Cit^-) may be more strongly specifically adsorbed on a positively charged electrode than the divalent ion, HCit^{2-} . One also expects this on the grounds that the more highly charged oxy-anion undergoes stronger interaction with water as demonstrated by its larger viscosity B-coefficient. Therefore, for the constant pH study of Na_2HCit , the values of $|q'_-|$ shown in figure (42) are smaller in magnitude than those for the variable pH study (figure (41)), because in the latter q'_- contains contributions from a greater proportion of H_2Cit^- ions.

The presence of H_2Cit^- may also account for the peak in q'_- versus q_m curves (variable pH study, figure (41)) which occurred at a smaller value of q_m than was observed in the corresponding results for the constant pH study (figure (42)). The occurrence of a peak in plots of q'_- versus q_m is rare for ionic adsorption, but has been reported for the p-toluene-sulphonate anion³² between $q_m = -2 \mu\text{C cm}^{-2}$ and $q_m = -6 \mu\text{C cm}^{-2}$. This is very similar to the value of electrode charge at which maximum adsorption takes place for many uncharged organic molecules¹⁰ (ie. $q_m \approx -2 \mu\text{C cm}^{-2}$). Results for trisodium citrate (see below) also have peak values of q'_- , but these do not occur until the electrode charge has reached more positive values; $q_m \approx 8 \mu\text{C cm}^{-2}$. As the ion valence varied

from -3 for Cit^{3-} to -1 for H_2Cit^- the adsorption behavior approached that characteristic of large organic ions (eg. p-toluene-sulphonate³²) or neutral organic molecules (eg. n-butanol¹⁰).

E. Trisodium Citrate

1. Primary Double Layer Results

Figure (43) shows a family of capacitance curves for trisodium citrate solutions which were obtained over the concentration range from 0.005M to the saturation limit, approximately 1.7M. The pH of each solution was measured and is given in Table XI. Data in figure (43) were recorded at a frequency of 35 Hz., however it was confirmed experimentally that capacitance results were independent of the superimposed a.c. signal frequency between 20 Hz and 1000 Hz. The capacitance minima for the three most dilute solutions occurred at potentials just negative of the p.z.c., as expected for unsymmetrical electrolytes²¹. A vertical line drawn through each curve in figure (43) identifies the p.z.c. The p.z.c. is also listed in Table XI on both the SCE scale (column two, $E_{(\text{SCE})}^{\text{p.z.c.}}$) and with respect to a sodium ion responsive electrode (column three, $E_{(\text{Na}^+/\text{Na})}^{\text{p.z.c.}}$). The capacitance at the hump was found to decrease in value with increased salt concentration greater than 0.10M. The capacitance measured at the p.z.c. is listed in Table XI for all concentrations. The trend of the capacitance values at the hump was contrary to that observed for most electrolytes, except at very high concentrations. This unusual result was the first indication that the structure of the double layer was possibly affected by ion-pair formation in the bulk solution.

Figure 43. Capacitance curves for Na_3Cit solutions: (a) 0.005M, (b) 0.010M, (c) 0.020M, (d) 0.050M, (e) 0.10M, (f) 0.20M, (g) 0.50M, (h) 1.00M and (j) approx. 1.7M, (saturated solution).

TABLE XI Double Layer Parameters For Na_3Cit at 25°C

conc.	$-E^{\text{p.z.c.}}_{(\text{SCE})}$	$-E^{\text{p.z.c.}}_{(\text{Na}^+/\text{Na})}$	$C^{\text{p.z.c.}}$	γ^{max}	pH
(mol l^{-1})	(mV.)	(mV.)	($\mu\text{F cm}^{-2}$)	(mNm^{-1})	
0.005	436.0	423	18.7	425.84	8.28
0.010	439.6	446	22.4	425.64	8.10
0.020	441.1	468	25.0	425.49	8.42
0.050	445.3	490	27.0	425.36	8.60
0.10	450.1	508	29.8	425.28	8.65
0.20	458.2	535	29.1	424.79	8.78
0.50	474.8	568	31.3	424.53	8.79
1.00	493.2	603	30.4	423.53	8.80
1.7 (Sat'd)	510.1	---	29.4	----	8.78

Integration constants for conversion of capacitance results to q_m and γ_c are given in Table IX (ie. $E_{(Na^+/Na)}^{p.z.c.}$ and γ^{max}). A complementary set of directly measured electrocapillary curves was obtained for the same conditions of pH and concentration as the data of figure (43), with the exception that no results were acquired for the saturated solution. In figure (44) the deviations between twice-integrated capacitance (γ_c) and measured interfacial tension (γ_m) are shown as a function of electrode potential, where $\Delta\gamma = \gamma_c - \gamma_m$. Only in the most dilute solution (0.005M and to a lesser extent in 0.010M) was there a significant discrepancy on the anodic branch of the electrocapillary curve (3.5 mNm^{-1} in 0.005M). For all other concentrations $\Delta\gamma$ was less than 1 mNm^{-1} up to 400 mV to 500 mV on the anodic side of the p.z.c. and $\Delta\gamma < 0.75 \text{ mNm}^{-1}$ on the cathodic side. Since the deviations were random for $c > 0.10M$, they are attributed to normal experimental error associated with the capacitance and electrocapillary methods of measurement. The level of error indicated is usually considered quite tolerable by experts who work in equilibrium double layer studies (eg. references: 20, 22,72,125). The presence of specifically adsorbed anions at $q_m = 0$ was noted by the shift of the p.z.c. to more negative electrode potentials (see Table XI, column two). The quantitative determination of anion specific adsorption from trisodium citrate will now be described in detail.

2. Anion Specific Adsorption

Anion relative surface excess, $\Gamma_{-(w)}$ was calculated from Parsons' auxiliary function, ξ_+ , as described in Chapter I. Mean

Figure 44. Comparison of directly measured interfacial tension (γ_m) and data obtained by double integration of capacitance curves (γ_c) as a function of electrode potential for Na_3Cit . $\Delta\gamma = \gamma_c - \gamma_m$.

molal activity coefficients for trisodium arsenate were used in the absence of data for trisodium citrate in the concentration interval examined. Kielland¹⁰² reported good agreement between his calculated individual ionic activity coefficients and experimental data of Bjerrum and Unmack¹³¹ for Cit^{3-} in dilute solutions ($c < 5 \times 10^{-3}\text{M}$). Experimental¹³¹ and calculated¹⁰² activity coefficients for PO_4^{3-} were about 10% smaller than those for Cit^{3-} at concentrations less than $5 \times 10^{-3}\text{M}$. The calculations of Kielland¹⁰² for mean molal activity coefficients were extended up to $c = 1\text{M}$ for Na_3Cit and compared with corresponding experimental data reported for Na_3PO_4 and Na_3AsO_4 by Harned and Owen^{81c}. Trisodium arsenate activity values were chosen in preference to those of Na_3PO_4 , because they were in closer agreement with the calculated results for Na_3Cit .

Diffuse layer anion charge, q_-^d , was evaluated as described earlier (Chapter I, Section E), and the charge due to specifically adsorbed anions, q_-^i was calculated, assuming cations were present only in the diffuse layer. The bulk dielectric coefficient, ϵ , used in the GCS calculations for q_-^d and q_+^d , was corrected for the effect of varying concentration by applying the relationship:

$$\epsilon = \epsilon_s + \left(\frac{\partial \epsilon}{\partial c} \right)_T c$$

where ϵ_s is the dielectric coefficient of pure water at 25° (ie. $\epsilon_s = 78.54$). The term $(\partial \epsilon / \partial c)_T$ was estimated as -19 mol^{-1} by comparison with other electrolytes given by Hasted and co-workers⁶⁰. The value of ϵ thus decreases to about 59 in a 1.0M solution.

Figure (45) is a plot of specifically adsorbed charge, q_-^i ,

versus the charge on the mercury electrode, q_m . These particular results were derived from electrocapillary data, because capacitance results extended to only about $q_m = 9 \mu\text{C cm}^{-2}$. Calculations of q'_- from capacitance results agreed with those in figure (45); the differences were greatest for the most concentrated solution and corresponded to a change in q'_- of about $\pm 1.5 \mu\text{C cm}^{-2}$. These errors are within tolerable limits, considering that the electrolyte is unsymmetrical⁸⁹. Some reasonable degree of confidence may therefore be given to the interpretation of the general shape of these curves. There is a significant amount of specific adsorption of citrate ions, which increases with concentration, but goes through a peak (ie. $|q'_-|$ is a maximum) for the more concentrated solutions at $q_m \approx 8 \mu\text{C cm}^{-2}$. This feature is of particular interest, because comparable results for the p-toluenesulphonate³² anion were shown to be caused by reorientation of adions, corresponding to a two-position adsorption model. That a similar interpretation does not apply in the present situation, is discussed in what follows. For 1.00M Na_3Cit , the peak occurs with $q'_- = -17.5 \mu\text{C cm}^{-2}$, which on the basis of the estimated ionic radius ($3.5 \text{ \AA}$) corresponds to only about 15% coverage of the electrode surface. In view of such small coverage, it is quite unlikely that repulsive ion-ion interactions would be large enough to enforce a reorientation of adsorbed anions. In addition, the approximately oval shape of the citrate anion does not suggest any particular parallel or perpendicular orientation would be preferred at the electrode. By contrast, the p-toluenesulphonate ion³² has an oblong shape, so that the ionic charge is located at one end of the adion remote from the benzene ring, and

Figure 45. Anion specifically adsorbed charge versus electrode charge for Na_3Cit .

one would actually expect preferred orientation under the stress of repulsive interactions. Parry and Parsons³² have demonstrated that when the electrode became crowded by adsorbed ions, a re-orientation occurred to permit further adsorption.

Attempts to fit the q'_- results for trisodium citrate to isotherms was unsuccessful, due to the curvature shown in figure (45). Consequently, the decrease in q'_- on either side of the maximum had to be explained in terms of ion-pairing effects in accordance with observations of a related nature found mainly in double layer electrode kinetics^{103,104} (see Chapter II).

The occurrence of a maximum in $|q'_-|$ curves (figure (45)) leads to considerations of electrical field effects on the nature of the adsorbed ions, rather than orientation phenomena. Besides this information, (ie. figure (45)), two additional calculations are worthy of inspection. These are (a) the potential developed across the inner layer^{16,32}, and (b) changes in dq_-/dq_m which are related to the Esin-Markov effect^{105,106}.

The implication of a maximum in the specifically adsorbed charge curves (figure (45)) is that at sufficiently large q_m the increased electrical field is exerting a major effect on the nature of the adion. The suggestion that it is the nature of the ion which is altered can be seen from further derived double layer characteristics shown in figure (46). Here the potential drop across the inner layer ($\phi_m - \phi_2$) has been plotted as a function of q'_- , using the methods of calculating $\phi_m - \phi_2$ described by Grahame¹⁰⁷ and Grahame and Parsons¹⁰⁸.

The plots are moderately linear at almost every value of q_m .

Figure 46. Calculated potential drop across inner layer vs. specifically adsorbed charge for Na_3Cit .

However, the slopes decrease as q_m increases. The reciprocal slope of the straight lines yields the capacitance of the inner layer due to specifically adsorbed anions: $q_-^i C$ (see ref. 16). Values of $q_-^i C$ are shown in figure (47) as a function of q_m . The rapid increase in $q_-^i C$ may be interpreted in terms of a decrease in the distance between the IHP and the OHP (ie. $x_2 - x_1$, see figure (1)). One expects ϵ to decrease as the field increases⁶³, so it is not likely that the very large values of $q_-^i C$ are to be rationalized in terms of a variation of the dielectric coefficient, especially since the capacitance is directly proportional to ϵ in the simple model of a parallel plate condenser. It is tempting to explain the tendency for $q_-^i C$ to approach infinity as a result of $|x_2 - x_1| \rightarrow 0$. The citrate ion, with its ionic charges localized at three spatially separated carboxyl groups, is probably much too complicated a species for application of a simple double layer model. The question arises as to the difficulty of assigning any meaningful value to the IHP distance x_1 , for a large, bulky organic ion¹³⁸. The problem is one of distinguishing between x_1 and x_2 in the case of a large, multiply charged ion, especially in the present case in which the coverage is so small (ie. a maximum value of ca. 15%). This makes it difficult to propose the existence of a well-defined inner plane for specifically adsorbed Cit^{3-} ions. A further complication is envisaged in the event that the anion undergoes a valence change either due to a dissociative field-effect or through formation of an ion-pair with a cation favorably located, say at the OHP. The result of such an event could be accompanied by a shift in the position of the IHP and/or the OHP, or it could be

Figure 47. Capacitance due to specifically adsorbed charge vs. electrode charge for Na_3Cit .

manifested by a change in the magnitude of the charge of specifically adsorbed anions, q_-' .

A second set of results, derived from double layer data, are shown in figures (48) and (49). In figure (48) the electrode potential (given with respect to the cation activity, E_+) is plotted against $\ln a_{\pm}$, for q_m between $8 \mu\text{C cm}^{-2}$ and $-10 \mu\text{C cm}^{-2}$. Presentation of data as shown in figure (48) is known as an Esin-Markov plot⁴⁵. The Esin-Markov coefficient, $(\partial q_- / \partial q_m)_{\mu}$, was calculated from the slopes of figure (48) through the relationships¹⁶:

$$q_- = z_- F \Gamma_{-(w)} \quad (10)$$

$$\text{and} \quad \left(\frac{\partial E_+}{\partial \mu_{\text{salt}}} \right)_{q_m} = - \left(\frac{\partial \Gamma_{-(w)}}{\partial q_m} \right)_{\mu_{\text{salt}}} \quad (73)$$

It was also calculated from the relative surface excesses ($\Gamma_{-(w)}$), and agreement of the two methods was good. In figure (49) $\left(\frac{\partial q_-}{\partial q_m} \right)_{\mu}$ is shown as a function of q_m . Grahame^{105,106} identified the Esin-Markov coefficient with $\tau_{\pm}$, the transference number of the ion (ie. τ_- for anions, τ_+ for cations), considering the e.d.l. to behave like a transport cell without charge transfer. At extreme positive and negative q_m , for 0.02M solution in figure (49), τ_- values are about unity and zero, respectively. For $c > 0.02\text{M}$, τ_- departs significantly from unity and zero at the extreme of q_m .

It is suggested that the adsorption behavior described above can be interpreted by considering the theoretical treatment of dissociative/associative effects in the double layer as proposed by Jenard and Hurwitz⁶².

Figure 48. Esin-Markov plot for Na_3Cit . Electrode charge indicated with each curve.

Figure 49. Esin-Markov coefficient as a function of electrode charge for five concentrations of Na_3Cit .

3. Ion Association Effects in the Double Layer

In their paper Jenard and Hurwitz⁶² have demonstrated that ion-pairing can, for certain electrolytes, predominate even in the presence of large electrical fields ($\approx 10^7$ volts cm^{-1}) which exist in the region of the OHP. In essence, the diagnosis of ion association does not rely merely on the concept of reduced electrostatic interactions with the OHP potential, ϕ_2 , owing to the decreased charge of the adsorbed species in the double layer. According to Jenard and Hurwitz, for aqueous electrolytes there may be the occurrence of water structure enforced ion-pairing in the electrical field. They contend that for fields less than about 10^6 volts cm^{-1} the Onsager dissociative effect prevails, but for larger field strength the reverse trend towards association dominates, depending on the abilities of the ions to interact with the solvent.

Aqueous trisodium citrate solutions have properties which conform to the requirements of the above theory. It has been shown through examination of the viscosity behavior that a large degree of structure-ordering occurs in Na_3Cit solutions. The results indicated that water is probably ordered by a large amount of hydrogen bonding between water molecules and the carboxyl groups of the Cit^{3-} ion. Thus the structural effects promoted by citrate and sodium ions agree in principle with the concept of Gurney⁴⁵ that interaction between oppositely charged ions increases if they both exert similar kinds of structural influence on the surrounding water molecules. It follows directly that ion-pair formation occurs in the homogeneous phase of solution. This is supported by the formation constants reported by Rechnitz and Zamochnick⁵⁴ and sodium ion

activity measurements discussed above in Section B.2. By inspection of the results in figure (46) it is possible to roughly estimate the magnitude of the electrical fields which are present when the mercury electrode is anodically polarized. If it is assumed that the OHP is located a distance of approximately, $x_2 = 4 \text{ \AA}$ from the interface, the field for $q_m = 8 \text{ } \mu\text{C cm}^{-2}$ would be about $6 \times 10^6 \text{ volt cm}^{-1}$ and for $q_m = 14 \text{ } \mu\text{C cm}^{-2}$ it would have increased to approximately $10^7 \text{ volt cm}^{-1}$. These calculations indicate that the electrical fields near the OHP are of about the intensity required by the predictions of Jenard and Hurwitz⁶². There are no data available on the molar or ionic depression of the dielectric coefficient of water ($\delta = (\partial\epsilon/\partial c)_T$) for Na_3Cit , Cit^{3-} or the ion-pair, NaCit^{2-} . The viscosity B-coefficients are not related in any simple way to the variation of $\bar{\epsilon}$ with different solute concentrations (c). From charge considerations alone it might be expected that $\delta_{\text{Cit}^{3-}}$ must be less than $\delta_{\text{NaCit}^{2-}}$ and since the value of $\delta_{\text{Na}^+} = -8 \text{ mol}^{-1} \text{ l}$ (ref. 60) one infers that the condition:

$$\delta_{\text{Cit}^{3-}} + \delta_{\text{Na}^+} \ll \delta_{\text{NaCit}^{2-}}$$

would prevail and hence justify the interpretation of the double layer results according to the theory of Jenard and Hurwitz⁶². It is now pertinent to re-examine those results, recognizing that both dissociative and associative processes are permitted in the inter-phase.

The slopes of the curves in figure (45) indicate that dq'/dq_m increases rapidly in the range: $-2 \text{ } \mu\text{C cm}^{-2} < q_m < 5 \text{ } \mu\text{C cm}^{-2}$. In this region of relatively moderate electric field, $\bar{F} \approx 10^6 \text{ volt cm}^{-1}$, ion-pairs (eg. NaCit^{2-}) will undergo field-assisted dissocia-

tion in accordance with predominance of the usual Onsager field effect. In the double layer this is seen as a competitive interaction, between Na^+ ions at the OHP and the positively charged electrode, for the charge on the Cit^{3-} ion. If field dissociation of NaCit^{2-} occurs, there will be a larger than expected accumulation of negative charge in the double layer. This kind of an effect is clearly depicted in figures (45) and (49) where dq_-'/dq_m and $(\partial q_-/\partial q_m)_\mu$ have their largest values; that is, over the q_m range: $-2 \mu\text{C cm}^{-2}$ to $5 \mu\text{C cm}^{-2}$.

Now, as the field increases for $q_m > 5 \mu\text{C cm}^{-2}$, it appears that reassociation has taken place. This is demonstrated by the fact that $|q_-'|$ goes through a peak value and then decreases again for larger q_m .

Maximization of the function: $\tau_- = (\partial q_-/\partial q_m)_\mu$ also lends support to the occurrence of such a phenomenon. That is, a decrease at higher q_m occurs in the overall rate at which negative charge is transferred into the double layer. It is also noted that the maximum in the value of $|q_-'|$ occurs at approximately the same value of q_m as the q_-' curve rises rapidly (see figure (47)) and where q_-' versus q_m has an inflection point (see figure (45)). In the present situation the steepness of the q_-' versus q_m curve suggests a rapid decrease in $|x_2 - x_1|$ due to ion-pairing at large q_m .

This discussion has been centered on the assumption that the ion-pair is NaCit^{2-} , but one cannot dismiss from consideration the presence of other more complicated species such as Na_2Cit^- or NaHCit^- 55, etc.

Another explanation may be that localized hydrolysis of the

citrate ion has occurred in the double layer. This would lead to formation of OH^- at the electrode, but on the basis of Payne's NaOH results²⁶ and those described for phosphates in Chapter V one would not expect to obtain such large q_m values, if such hydrolysis did take place. It is not possible to exclude multiple association of adions at large q_m , but a firm conclusion of this cannot be inferred from the present results.

Results for disodium citrate may also be discussed in terms of the Jenard-Hurwitz treatment. The peak in the q'_m curves (figures (41) and (42)) can be attributed to existence of a field-dissociated ionic species which may reassociate in a stronger field; this situation being analogous to that described for trisodium citrate. Definite conclusions cannot be made as to the identity of the associated species. It may be either HCit^{2-} or an ion-pair, such as NaHCit^- , for which some evidence exists in the literature⁵⁵. If the ion-pair is the species which prevails in the bulk of disodium citrate solutions, and is field-dissociated in the interphase, then this supports the fact that $\Gamma_{-(w)}$ values were larger for disodium citrate solutions than for trisodium citrate, for $q_m > 0$. This implies that the dissociated species in disodium citrate solutions (ie. HCit^{2-}) is more strongly adsorbed on positively charged mercury than is the dissociated species from trisodium citrate solutions (ie. Cit^{3-}). The fact that peak values of q'_m occurred for smaller q_m in disodium citrate than in trisodium citrate may also indicate that the NaHCit^- ion-pairs is weaker than the NaCit^{2-} ion-pair.

A comparison of q'_m versus q_m curves for 1.00M solutions of widely differing pH has been made in figure (50). These results

Figure 50. Comparison of plots of anion specifically adsorbed charge versus electrode charge for 1.00M sodium--citrate solutions at three different pH values.

represent an interesting feature of the citrate system, namely that for $q_m \approx 15 \mu\text{C cm}^{-2}$ the amounts of charge due to specific adsorption of anions (q'_i) are relatively constant. From the calculations shown in figure (31) one should expect a variable mixture of adsorbed species at the electrode, (ie. H_3Cit , H_2Cit^- , HCit^{2-} and Cit^{3-}), but since the curves at pH = 4.63, 5.57 and 8.8 merge at extreme anodic charges it may be speculated that very strong electric fields, say $\bar{F} > 10^7 \text{ volt cm}^{-1}$, affects the double layer composition to the extent that there may be a common set of "complexed adions" when $q_m \approx 15 \mu\text{C cm}^{-2}$. It is pertinent to mention that the same type of behavior is observed for solutions more dilute than those of figure (50). In fact, for solutions down to 0.2M, the amount of specific adsorption is constant at extreme positive values of q_m .

4. A Proposed Model and Supplementary Work

It is difficult to speculate on all the possible microscopic effects concerning the structure of the double layer for anion adsorption from citrate solutions. The principal results derived from interpreting double layer and solution behavior for Na_3Cit are summarized in a schematic molecular model shown in figure (51). The Cit^{3-} ion may be adsorbed on the electrode surface in either of configurations A or B. The latter would appear to be a more realistic model, because it allows all three carboxyl groups to freely interact with neighbouring water molecules and thereby contribute to the promotion of hydrogen bonding in the double layer. Model B in figure (51) therefore is intended to convey pictorially the microstructure of the interphase in the low field condition when

Figure 51. Schematic diagram for adsorbed Cit^{3-} at a mercury electrode.

the Onsager dissociation effect prevails. In C, the adsorbed citrate ion is in the B configuration, indicating most favorable possibilities for water enforced ion-pairing with hydrated sodium ions. Overlapping of cospheres of hydration of Cit^{3-} and Na^+ in the double layer are not depicted in figure (51) but is likely to occur in the event of ion-pair formation.

It was mentioned previously (Section E.1) that lowering of the capacitance hump observed for the most concentrated solutions was probably related to the presence of ion-pairs. Results obtained in the present work tend to support the view that the hump is primarily due to the freedom of reorientation of electrode bound water. Lowering of the hump for most concentrated solutions of Na_3Cit may result from a decrease in ion-dipole forces between contact-adsorbed Cit^{3-} and water molecules at the interface. This is brought about by a partial cancellation of the negative charge on the anion through formation of an ion-pair with Na^+ at the OHP. The effect is enhanced in concentrated solutions due to structure enforced ion-pairing and therefore a water molecule on the electrode surface experiences a less restrictive environment and can rotate more freely.

Supplementary experimental work was done to further investigate the effect of ion-pairing on capacitance results. Since ion-pair formation constants, reported for the different alkali metal citrates, depended on the nature of the cation some capacitance curves were obtained to investigate the possibility of detecting these differences. The results are shown in figure (52) for 0.10M solutions of Li_3Cit , Na_3Cit , K_3Cit and $(\text{NH}_4)_3\text{Cit}$. The differences

Figure 52. Comparison of capacitance curves for 0.1M solutions of: Na_3Cit (a), K_3Cit (b), $(\text{NH}_4)_3\text{Cit}$ (c) and Li_3Cit (d).

between the curves for the various solutions were within the range of experimental error, as given in Chapter IV. The accuracy of capacitance measurements would have to be improved greatly to detect the small differences which may exist as a result of varying degrees of ion-pairing.

Campi and co-workers⁵⁶ reported on the stability of complexes of tricarballic (ie. 1,2,3 propanetricarboxylic) and citric acids with bivalent metal ions. Tricarballic acid has a hydrogen atom instead of the alcoholic hydroxyl group present in the citric acid molecule. Campi et al. showed that the complexes with citric acid were slightly more stable than those with tricarballic acid due to the hydroxyl group. On this basis, ion-pairing with alkali metal cations should be less for salts of tricarballic acid than for corresponding salts of citric acid.

Some tricarballic acid was purified from diethyl ether in a soxhlet extraction apparatus and a solution of trisodium tricarballylate (0.10M) was prepared by adding NaOH. The solution was made up to pH = 8.05. Capacitance results for the 0.10M solution of trisodium tricarballylate are shown in figure (53) and the corresponding data as given for 0.10M Na₃Cit. The differences between the two curves are appreciable and on a qualitative basis suggest that the tricarballylate anion is probably more strongly adsorbed than Cit³⁻ at potentials more positive than the p.z.c. It is clear that the absence of the hydroxyl group in the tricarballylate ion has a greater influence on the double layer properties of this anion compared to the negligible effect of varying degrees of ion-pairing on the capacitance curves observed for Li₃Cit, Na₃Cit and K₃Cit.

Figure 53. Comparison of capacitance curves for 0.1M solutions of Na_3Cit (a) and $\text{Na}_3\text{Tricarballoylate}$ (b).

Capacitance curves were also obtained for a wide range of concentrations of Li_2SO_4 , Na_2SO_4 and MgSO_4 , but results were often not reproducible in the region of the capacitance hump. These difficulties were most apparent for MgSO_4 solutions for which a typical capacitance curve has been plotted in figure (54). The irregular peaks on the capacitance curve near the hump are spurious. The sulphate salts investigated in these studies were of highest chemical purity and were further purified by recrystallization. The source of the problem could not be attributed to water impurities since good results were obtained for even the dilute citrate solutions and 0.01M KCl. An unidentified impurity in the MgSO_4 reagent was probably the cause of the poor results. It would be very interesting to compare double layer results for MgSO_4 with those reported for Na_3Cit in view of the well known presence of strong ion-pairing⁵⁸ in MgSO_4 ($K_f = 234 \text{ mol}^{-1} \text{ l}$) and the high degree of structure-ordering caused by both Mg^{2+} and SO_4^{2-} ions. For example viscosity B-coefficients are⁴⁴: $B = 0.434$ for Mg^{2+} and $B = 0.204$ for SO_4^{2-} . Double layer studies have been published (eg. ref. (34) and (40)) for the Hg electrode/ MgSO_4 solution interphase, but results of the type found here for Na_3Cit have not been reported. Failure to resolve the experimental difficulties encountered in capacitance work for solutions of MgSO_4 is regrettable, but it serves to emphasize that very high standards of purity were required to ensure reproducibility of double layer data. The results presented in this thesis can therefore be regarded with confidence since use of the Kowalski-Srzednicki instrument has proved to be a very sensitive means of detecting minute irregularities in capacitance data.

Figure 54. Capacitance curve for 0.015M MgSO_4 , typical of results obtained for this salt. Broken part of line indicates the nature of non-reproducible capacitance behavior.

The interpretation given above for the Na_3Cit results, in terms of dissociative and associative effects in the double layer as proposed by Jenard and Hurwitz⁶², have recently been published¹¹⁶.

CHAPTER VIISUMMARY

An extensive experimental study was made of electrochemical adsorption of sodium salts of orthophosphoric and citric acids. Viscosity and density data were obtained to provide information regarding structural properties of the various phosphate and citrate ions in the homogeneous phase of electrolyte solutions. Double layer experiments included both interfacial tension and differential capacitance measurements which were obtained for the heterogeneous mercury electrode - aqueous solution interphase. Accurate potentials of zero charge were measured by the streaming mercury electrode method for all solutions examined. In order to detect ionic specific adsorption at the uncharged mercury electrode the streaming potentials were measured with respect to a constant activity reference electrode, the SCE. The potential of a sodium ion responsive glass electrode was measured in all solutions to provide a thermodynamically reversible scale of electrode potentials and to investigate the presence of ion-pairs in citrate solutions. Interfacial tension and capacitance results were both analyzed using double layer thermodynamic treatments with the aid of digital computing methods.

Large differences between directly measured interfacial tensions and those derived from capacitance curves were observed only for Na_3PO_4 solutions. These discrepancies, associated with sticking of the mercury meniscus in the Lippmann electrometer at extreme anodic potentials, were attributed to possible formation of highly insoluble mercury compounds such as: $(\text{Hg}_2)_3(\text{PO}_4)_2$, Hg_2HPO_4 and HgO .

The charge due to specifically adsorbed ions was calculated by

comparing experimental relative surface excesses with the predictions of the Gouy-Chapman-Stern diffuse layer theory. The p.z.c. for Na_2HPO_4 and Na_3PO_4 solutions, over the entire range of concentrations investigated, varied by less than one millivolt. No anion specific adsorption was detected for Na_2HPO_4 or Na_3PO_4 until positive electrode charges were attained, and then q'_- increased rapidly. Results of q'_- calculations were compared with those published for other related ionic systems, such as: NaH_2PO_4 , NaF and Na_2SO_4 .

The presence of an ion-free layer of adsorbed water molecules was considered to exert an appreciable influence on the calculated values of q'_- , and this concept was subsequently employed to obtain "corrected data" for anion specific adsorption from phosphate salt solutions. Results for Na_3PO_4 were shown to be affected by the presence of hydroxyl ions. It was proposed that the adsorbability of the different phosphate anions on positively charged mercury was related to the high degree of structure-ordering caused by these oxy-anions in aqueous solution, as indicated by their large, positive viscosity B-coefficients. Increasing specific adsorption was suggested to occur in the order: $\text{PO}_4^{3-} < \text{HPO}_4^{2-} < \text{H}_2\text{PO}_4^-$, on a positively charged mercury surface.

The very steep rise of the anodic capacitance for Na_2HPO_4 and Na_3PO_4 was discussed in terms of rapidly increased specific adsorption of HPO_4^{2-} , PO_4^{3-} and OH^- ions for increased positive electrode charge. The absence of a hump in the capacitance curves was considered to be due to strong interaction between phosphate ions and inner layer water molecules which opposed reorientation of the

adsorbed water dipoles in the increasing field of the electrode. A possible model of the interphase was proposed to account for the observed double layer properties.

Initial work on citrate solutions revealed very complicated double layer behavior. Attention to the homogeneous properties of solutions, especially in regard to co-existence of a variety of ionic species, was considered of primary importance to understanding the diversity of possible interactions in the mercury-electrolyte interphase. A qualitative and comparative interpretation of the preliminary capacitance results showed that Cit^{3-} was adsorbed on a positively charged electrode somewhat more strongly than SO_4^{2-} , but less than ClO_4^- . Among the different citrate ions, specific adsorption at anodically polarized mercury was found to take place in the sequence: $\text{Cit}^{3-} < \text{HCit}^{2-} < \text{H}_2\text{Cit}^-$, which is analogous to the order proposed for phosphates. This similarity of adsorption behavior for the two different types of oxy-anions was attributed to the very strong ordering of the water structure common to both citrates and phosphates.

Slow attainment of adsorption equilibrium for H_2Cit^- and/or undissociated citric acid did not permit the recording of reproducible and accurate capacitance curves from citrate solutions with $\text{pH} < 4.5$, and therefore, subsequent double layer studies were confined to solutions of Na_2HCit and Na_3Cit .

Disodium citrate solutions whose pH was controlled at $\text{pH} = 5.5$ gave different interfacial tension and capacitance results than those solutions in which pH varied between 4.63 and 5.36 as a function of concentration. Calculated q'_l values were interpreted

with caution due to the questionable validity of applying diffuse layer theory to such complex mixtures of ions of different valency. The results for disodium citrate solutions indicated on a semi-quantitative basis stronger adsorption of H_2Cit^- than the divalent ion, HCit^{2-} .

Attention was focussed mainly on the study of citrate solutions with $\text{pH} > 8$ in which the predominant citrate species was Cit^{3-} . From viscosity measurements it was shown that Cit^{3-} behaved as a water structure-ordering centre. Ion-pairing with Na^+ was enforced since both anion and cation exerted a similar effect on the structure of water. A large value for the viscosity A-coefficient ($A = 0.04$), confirmed by Na^+ activity measurements, supported published evidence that NaCit^{2-} ion-pairs were present in the homogeneous solution phase.

Analysis of double layer results for Na_3Cit showed the presence of a peak in the plot of q'_- versus q_m , which could not be explained by invoking a two-point adsorption model for reorientation of adsorbed ions. The capacitance due to specifically adsorbed charge was found to increase rapidly in the region, $q_m \approx 8 \mu\text{C cm}^{-2}$, where q'_- results showed a peak value. Esin-Markov plots were also examined and revealed, in conjunction with the above results, that ion-pairing effects were occurring in the double layer as well as in the bulk solution.

The experimental findings on the nature and behavior of adsorbed species in the interfacial region could be accounted for by considering electrical field-assisted dissociation and association effects according to a theoretical treatment by Jenard and Hurwitz. In

electrical fields present near the OHP for small q_m ($\bar{F} \approx 10^6$ volts cm^{-1}), the Onsager dissociation effect was predominant and caused NaCit^{2-} ion-pairs to be field-dissociated. In larger fields (eg. $\bar{F} > 10^7$ volt cm^{-1}) operating at more positive q_m , an associative phenomenon took place in which adsorbed citrate ions underwent reassociation with Na^+ ions located at the OHP. A modelistic molecular representation of the double layer was proposed in accordance with the interpretation using the theory of Jenard and Hurwitz. The Cit^{3-} ion was assumed to adsorb with its alcoholic hydroxyl group towards the metal surface in a configuration favorable for maximum participation of the citrate charge centres in hydrogen bonding with water and ion-pairing with sodium ions located near the OHP. Peak values of q'_- for disodium citrate solutions were also attributed to associative-dissociative interactions, possibly involving species such as NaHCit^- ion-pairs. Comparison of $q'_- - q_m$ curves for disodium citrate and trisodium citrate suggested the possibility in the case of very large fields (ie. for $q_m > 15 \mu\text{C cm}^{-2}$) of a common set of complexed adions.

The work described in this thesis is to the author's best knowledge the first attempt to investigate double layer properties of unsymmetrical, 1:3 electrolyte types. It was demonstrated that comparison of data measured by interfacial tension and capacitance methods should be made wherever possible to ensure that dependable data are obtained. The use of an automatic capacitance recording technique was found to be very useful as a means of rapidly detecting difficulties due to solution impurity or slow adsorption behavior, effects which could go unnoticed in electrocapillary measurements.

Interpretation of ionic adsorption in the heterogeneous interphase between the electrode and solution was aided by considering bulk solution properties derived from viscosity, density and cation activity measurements. The most important contribution of fundamental interest to double layer studies was the direct experimental evidence in agreement with the theory proposed by Jenard and Hurwitz. Although dissociative effects have been shown to occur in the double layer, the results discussed in this dissertation are the first direct proof of ion-association near the electrode surface. They also serve to emphasize the importance of structural effects in the double layer due to the combined influences of ionic and electrode fields.

It is hoped that the study presented in this thesis has not only fulfilled the author's concern for scientific curiosity and academic scholarship, but has also offered some basic information of use to other research workers. In particular the results may be helpful to those involved in understanding and resolving some of the problems of great complexity related to pollution of inland and coastal waters.

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