ORIENTATED WATER UNDER INSOLUBLE MONOLAYERS

a Thesis presented for the degree of Master of Science in the Department of Physical Chemistry at Melbourne University.

by

JOHN RALSTON

August, 1970.
"Utram bibis? Aquam an undam?"

— source unknown.

literally:-

Which are you drinking? The water or the wave?
In the development of the ideas in this thesis I owe much to a number of people.

My supervisor, Dr. T.W. Healy has provided me with a large amount of help and advice in many ways, particularly at times when my morale had begun to ebb. I feel privileged to have worked with him as a research student, especially since he encouraged independent thought at all times, the result of which has been some interesting discussions.

Over a period of several years, David, Bob, Graham, Andrew, Brian and Stephen have provided help in things chemical and otherwise — I'm glad to have worked with them.

My wife Ann has been remarkably good humoured and tolerant during the period that this thesis was written, despite the fact that it coincided with the early months of our marriage.

My father has also aided me in many small, but valuable ways, making the transition from rough draft to final copy a speedy one.

Helen George has, by some magical sixth sense, managed to type this thesis from my impossible writing and to her I offer my sincere thanks.

Finally I would like to thank Mobil Oil Australia Ltd. for the award of a Research Scholarship.
## INDEX

### CHAPTER I
- **INTRODUCTION** 1

### CHAPTER II
- **REVIEW**
  - (i) Water Properties 4
  - (ii) Monolayer Properties 16

### CHAPTER III
- **EXPERIMENTAL PROCEDURE** 24

### CHAPTER IV
- **RESULTS** 34

### CHAPTER V
- **DISCUSSION**
  - 5.1 The Surface Tension of Salt Solutions 55
  - 5.2 Equilibrium Spreading Pressures of n-octadecanol. 66
  - 5.3 The Surface Pressure-area/molecule isotherms for n-octadecanol on various substrates. 70
  - 5.4 Thermodynamic Analysis of Pressure/Area Data. 75
  - 5.5 General Discussion. 81

- **SUMMARY** 89

- **FUTURE WORK** 90

- **APPENDICES** 91

- **REFERENCES** 106
1.

CHAPTER 1. INTRODUCTION

The fact that oil could calm a rough sea was recorded by Pliny the Elder and by Plutarch. More quantitative information was provided by Benjamin Franklin in 1774 when he reported to the Royal Society that a teaspoonful of oil made a half-acre surface of pond ".... as smooth as a looking glass" (24). Subsequent experimentation showed that a similar effect could be observed when small amounts of insoluble soaps or "fatty" organic compounds were spread on water surfaces. Willard Gibbs published his thermodynamic treatment of surface tension and adsorption in 1878, providing the necessary theoretical background for explaining experimental results (66). In 1891 Fraulein Pockels developed the technique of manipulating these insoluble films between "barriers" extending across the entire width of a trough of water, filled so that it almost overflowed. This permitted quantitative information about surface tension and surface area to be obtained and led Rayleigh to propose, in 1899, that surface films were only one molecule thick. The basis for contemporary understanding of the behaviour of molecules in insoluble monolayers was provided in 1817 by Irving Langmuir (97), who devised the surface balance which still bears his name and whose results verified the theories of molecular orientation at surfaces.

Certainly many characteristics of monomolecular films, or monolayers as they are more usually called, are well understood. However certain features still remain uncertain. For example, monolayers "organize" or "structure" the water directly underlying them (101, 102), however very little is known about the nature of this orientated interfacial water. The paucity of knowledge about interfacial water is certainly not restricted to this system alone; very little is known about it at the solid-liquid, liquid-liquid or liquid-air interfaces in general, though a large amount of partially explained quantitative information abounds. Recent
2.

papers by Derjaguin (5) and Drost-Hansen (12 to 17), the first involving the concept of a new type of water condensed in quartz capillaries and the second concerning structured interfacial water, have resulted in a good deal of interest in this topic. Moreover the possibility that structured water may exist in cell membranes (11) stresses the importance of this subject, since it could probably help to explain both ion transport and cell membrane operation in the body.

It has been well established (77) that different ions have opposing effects on bulk water structure. "Structure-breaking" ions such as K\(^+\) and Cs\(^+\) disrupt the water structure whilst "structure-making" ones like Mg\(^{2+}\) and La\(^{3+}\) enhance it. K\(^+\) and Na\(^+\), for example, are present in moderately high concentrations in the human body and, noting that phospholipids and steroids, which are known to be the major constituents of cell membranes, form insoluble films on water, it would appear that a knowledge of the effect of electrolytes on the orientated water beneath insoluble monolayers is potentially very useful in explaining a variety of phenomena. A veritable mine of information exists on the physical and chemical properties of monolayers on various liquid, mainly aqueous, substrates (see Chapters 2, 5). The action of electrolytes on the properties of ionizable monolayers is generally attributed to electrostatic interaction between the ionized head groups and the respective ions in the aqueous subphase (37, 41); results due to interfacial water structure are normally neglected. To date there has been almost no work performed on the effect of electrolytes on unionized monolayers (e.g. long chain alcohols), for which electrical effects will be minimal, the major changes being related to the action of the electrolytes on the interfacial water and the OH dipole of the long chain alcohol. Effects due to dilute salt solutions are expected to be small and have been disregarded by other workers (59).
On the other hand, one might expect concentrated solutions of structure makers and breakers to exhibit some influence on the interfacial region. A straightforward method of detecting such phenomena involves the determination of the surface pressure-area per molecule characteristics of unionized, insoluble monolayers on the various substrates concerned. Provided one can choose a substance whose pressure-area characteristics on pure water are well known, one has an ideal reference with which to compare the effect of different electrolytes added to the water.

Pre-empting the comments made in later sections on the difficulty of proposing a definite, precise structure of bulk or interfacial water, the aim of the investigation reported here was to obtain and analyse quantitative information on the influence of electrolytes on interfacial water under insoluble, unionized monolayers of the long chain alcohol n-octadecanol.
CHAPTER 2. REVIEW

1. WATER PROPERTIES

(a) Interfacial Structure

The existence and extent of enhanced liquid structure at an interface (liquid-liquid, liquid-solid or liquid-gas) is subject to a good deal of conjecture. Although ordered interfacial structure has been proposed for many years, only recently have there been any attempts to examine its structure (34, 33, 50, 5). In the present investigation the nature of the air-water interface has been considered, but information concerning other types of interfaces may also elucidate some of the problems involved.

Henniker (1) has reviewed in detail the experimental data relating to the depth of the surface zone of a liquid at a liquid-gas interface. Citing direct evidence such as x-ray diffraction, electron diffraction, surface viscosity measurements etc. as evidence for deep surface orientation, Henniker explains general physico-chemical data such as vapour pressure and elasticity in terms of a structured surface layer. His concept is that strong, short range intermolecular forces are transmitted by polarization of neighbouring molecules to a significant distance from the interface into the liquid. For instance a comparison between the viscosity of an oil near a solid surface with that in the bulk showed that, depending on the oil type, there was an increase (up to tenfold) in viscosity within 1000 A to 5000 A of the wall (2). This effect was interpreted as a preferential development of structure near the oil/metal interface. Furthermore there have been numerous observations (3) that the physical properties (e.g. melting point) of relatively thick films adsorbed on to metal surfaces differ considerably from the corresponding bulk properties. When certain inorganic sols coagulate
5.

(e.g. iron oxide, tungsten trioxide), ordered Schiller Layers (4) originate and the particles arrange themselves in horizontal layers on settling which are separated by water layers thousands of Angstroms thick, the long range interaction forces between the colloidal particles acting over a considerable distance.

Recently there has been a considerable amount of study of the properties of water condensed into quartz capillaries and a new type of water termed "orthowater", "anomalous water", "super water" or "polywater" has been proposed (5, 6, 7, 8). This orthowater is 12 to 15 times more viscous than normal water, is 40% denser and has a lower vapour pressure. The extensive ordering in this orthowater is supposedly produced by the interaction of water molecules with both the silicate surface and each other. In normal water, orthowater behaves like a separate, highly soluble substance, in that it separates out on cooling or is left as a residue when normal water is pumped off. At present the structure most compatible with experimental evidence is an ice\textsuperscript{II} like structure (8). The major criticisms of the existence of this water are that it may be a silica dispersion (9) or that surface tension gradients may explain the different physical properties (10). A complete understanding of its nature is of great importance since the capillary structure of living cells may contain anomalous water (11).

Drost-Hansen has made numerous contributions to the nature of water at water/air and water/solid interfaces (12 to 16). From a study of the thermal anomalies (or "kinks") appearing in temperature coefficient measurements performed on water, Drost-Hansen has proposed that an ordered region of considerable depth (e.g. 10 to 20 molecular layers (12) ) exists at the water-air interface. The "kinks" appear in
viscosity, magnetic susceptibility, specific heat, NMR and surface tension measurements performed as a function of temperature, to mention but a few. They are interpreted in terms of structural changes occurring at the particular interface concerned and appear at approximately 15°, 30°, 45° and 60° C. Recently (17) Drost-Hansen has suggested that where claims have been made for the presence of "kinks" in bulk water properties, the results may in fact be due to structured interfacial water, which is expected to have specific thermal stability limits. It must be emphasised that to irrevocably solve the problem of thermal anomalies in, for example, surface tension measurements, an extremely accurate set of data is required. To this end Gittens (18) and Cini, Loglio and Ficalbi (19) have measured the surface tension of water over small temperature intervals, both groups of workers taking great care in the experimental arrangements. The former concludes that thermal anomalies are absent, the latter that they are present. To clarify the issue completely Gittens remarks that surface tension measurements accurate to at least 0.001 dyne cm⁻¹ are necessary. Further O'Neil and Adami (20) find no thermal anomalies in the temperature dependence of the oxygen isotope partition function ratio of liquid water.

In direct opposition to the above, Falk & Kell (75) question the whole idea of kinks and attack infra-red, molar volume and bulk compressibility data on two grounds. Firstly they point out that the error ranges quoted in these experiments are of the same order of magnitude as the step-like discontinuities reported, and there is therefore no sound reason for regarding them as kinks. Secondly the thermal anomalies have been reported over a wide range of temperatures (e.g.
Qurashi (124) reports eleven kinks in viscosity measurements between 6°F and 60°F, inferring that they may be merely artifacts. From these latter works it is obvious that some confusion remains over the interpretation of kinks.

As further evidence for the existence of structure at interfaces, Horne (34) has examined the properties of particulate solids in aqueous solutions and concludes that a perturbed water structure exists, extending out from the surface for several microns. The use of polarized light (76) has yielded a minimum value of 7Å at 0°C for the thickness of the surface zone of water at the water/air interface. Good (96) considers that the "normal" surface entropy for non-hydrogen bonding liquids (based on an average for a large number of substances), minus that for strongly hydrogen bonding liquids, is a measure of the surface orientation. For water, Good's results indicate that orientation exists in at least the 3rd layer of water molecules near the air/water interface. Hence one can assume that the surface layers of a liquid possess a definite structure, the extent of which is uncertain; this is in contrast to the classical view of very limited or monolayer orientation. The nature of this structure is poorly understood and is considered again in Chapter 5.

(b) Bulk water structure

The inherent difficulties in examining the nature of interfacial water can be highlighted by briefly covering the ideas associated with the structure of bulk water (77, 78).

Early models of liquid water (79) pictured it as a mixture of small aggregates (i.e. of H₂O, (H₂O)₂, (H₂O)₃ etc.) The dependence of properties on temperature, pressure and solute concentration was explained by changes in the equilibrium concentrations of the aggregates.
and for many properties a good fit between theory and experiment was achieved. In 1933 Bernal and Fowler (80) interpreted X-ray diffraction measurements on liquid water in terms of an extended but irregular tetrahedral arrangement of water molecules; they criticised the small aggregate models as providing an incorrect description of the spatial arrangement of the molecules in the liquid. A similar interpretation was advanced by Morgan and Warren (81) in 1938, both groups of workers suggesting a similarity between the structure of liquid water and that of ice.

From these early deliberations, numerous theories of bulk water have been advanced, the authors attempting to define the situation in more detail. These proposals can be broadly categorized into two sections:

A. mixture models, where the liquid is seen as a group of differently hydrogen bonded species in which each water molecule can alternate through states where none, one or both of its hydrogens are engaged in hydrogen bonding.

B. continuum models, where water is treated as a three dimensional lattice of tetrahedrally co-ordinated, hydrogen bonded molecules. Bond breakage apparently does not take place. Hydrogen bond stretching and bonding deformations are supposedly produced by electrostatic, thermal and steric perturbations.

The fundamental premise in mixture models is that water is composed of a small number of molecular species, each species occupying a certain state or energy level. Thermal agitation causes frequent transitions between states, thus all molecules are effectively equivalent over a period of time. Temperature and pressure changes cause shifts in the relative populations of the states, consequently leading to the explanation
of thermodynamic properties. Of the considerable number of mixture models that have been proposed to characterize the structure of bulk water, the vacant lattice point model of Forslind (82, 83) and Frank and Wen's (84) so called "flickering cluster" are perhaps the best two examples. The first of these considers water to be a tetrahedrally extended, crystalline system containing interstitial cavities of sufficient size to accommodate free, non-associated water molecules. Dissolved electrolytes are regarded as producing lattice distortions due to steric and electrostatic effects. The second model proposes the existence of flickering clusters of water molecules, of relatively short lifetime, formed by a co-operative hydrogen bond making/breaking process in water.

Infra-red and Raman vibrational spectroscopic data (85, 86) provide the strongest case for a continuum model of water structure, since the spectra indicate a continuous distribution of hydrogen bonded energies. Pople (87) is a further proponent of this model, since the observed variation of the X-ray radial distribution function can be explained by the continuum idea.

Certainly there is a wealth of ideas and experimental data pertaining to the structure of bulk water. Holtzer and Emerson (125) demonstrate that for aqueous solutions of proteins and small molecules such as urea, the interpretation of experimental data in terms of water structure can lead to ambiguous conclusions. Although the variation of certain specified parameters with temperature, pressure etc. can be explained by a given model, not one can satisfactorily explain all the properties of water, this apparently simple liquid. At this stage it seems that the unhappy situation of a large number of competing models will prevail for some time to come.
The effect of dissolved electrolytes on the structure of water.

The structure of water is considerably modified in ionic solutions, due to the presence of ions possessing both size and charge. There is a very strong electric field associated with an ionic charge and this must be accounted for when considering the interaction between solute and solvent. In dilute solutions the average separation of ions is large enough to allow the effect of a single ion on adjacent layers of water molecules to be considered, however this is not the case in concentrated solutions. For a 1:1 electrolyte at 1 molar, the average separation is 9.4 Å whilst at 0.1 molar it is 20 Å. Therefore one can only talk of "unperturbed" water structure at concentrations below 0.1 molar; in more concentrated solutions essentially all the water is influenced by the ions.

Ions can be broadly classed as "structure makers" or "structure breakers", a classification which is based on the relative strengths of their respective electric fields (77). Due to their high electric fields, relatively small and multivalent ions such as Li⁺, Na⁺, H₃O⁺, Ca²⁺, Mg²⁺, Al³⁺, OH⁻ and F⁻ induce additional order beyond the primary hydration sheath of water molecules and are consequently referred to as structure makers. Ions such as K⁺, NH₄⁺, Rb⁺, Cs⁺, Cl⁻, Br⁻ and ClO₄⁻ have a relatively weak electrostatic field and influence water molecules only in the first layer. Beyond this layer they actually disrupt or "break" the water structure and are thus referred to as "structure breakers". For ions such as (C₂H₅)₄N⁺, (C₃H₇)₄N⁺ etc. there is virtually no attraction of the ion surface for water molecules and they are essentially unhydrated. These species are in fact too large to permit the water structure to collapse about them and generally increase the structure or ordering of the bulk solution.
Whether or not an ion is a structure maker or breaker may be decided on the basis of a variety of experimental evidence. Although the broad trends indicated by the various techniques generally agree, discord is often exhibited for individual ions. The Jones-Dole equation (88) depicts the influence of a strong electrolyte on the viscosity of a solvent.

\[
\frac{\eta}{\eta_0} = 1 + A\sqrt{C} + BC
\]

where \(\eta/\eta_0\) is the viscosity of the salt solution relative to that of the solvent water, C is the molar concentration and A, B are constants. The B coefficient represents a measure of the ion-solvent interaction, positive values of B generally being associated with structure making and negative values with structure breaking (89). More precise information concerning the enhancement or disruption of the solution structure is provided by the temperature dependence of the B coefficient, obtained through a study of the activation energy for viscous flow, \(\Delta E^\ddagger\), of a solution containing a strong electrolyte (89). Negative values of \(\Delta E^\ddagger\) for a specific ion correspond to structure breaking and positive values to structure making (refer Table 2.1).

Entropy is a useful criterion for judging the degree of structural organization of water in ionic aqueous solutions. Partial molar/molal entropies are readily accessible, however to obtain the actual effect of the solute on the solvent structure, certain features must be considered. The entropy specifically connected with a solute and its associated cosphere of water is termed by Gurney (90) the partial molal unitary entropy of solution, \(\Delta S^\ddagger\) unitary. This quantity is obtained by separating the "cratic" part, representing the composition and amount of solution, from the conventional partial molal entropy of solution \(\Delta S^\ddagger\).
### TABLE 2.1 SELECTED B COEFFICIENTS AND ACTIVATION ENERGIES FOR VISCOUS FLOW AT 25°C (From Refs. 89, 94).

<table>
<thead>
<tr>
<th>ION</th>
<th>Bi mole⁻¹</th>
<th>ΔEᵢ, cal mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Structure Makers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li⁺</td>
<td>+0.150</td>
<td>+210</td>
</tr>
<tr>
<td>Na⁺</td>
<td>+0.086</td>
<td>+20</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>+0.385</td>
<td>+420</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>+0.285</td>
<td>-</td>
</tr>
<tr>
<td>Ce³⁺</td>
<td>+0.576</td>
<td>+390</td>
</tr>
<tr>
<td>F⁻</td>
<td>+0.096</td>
<td>+1240</td>
</tr>
<tr>
<td>(C₂H₅)₄N⁺</td>
<td>+0.385</td>
<td>+160</td>
</tr>
<tr>
<td>(n-C₃H₇)₄N⁺</td>
<td>+1.092</td>
<td>+620</td>
</tr>
<tr>
<td><strong>Structure Breakers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>-0.007</td>
<td>-100</td>
</tr>
<tr>
<td>K⁺</td>
<td>-0.007</td>
<td>-220</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>-0.030</td>
<td>-490</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>-0.045</td>
<td>-430</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>-0.007</td>
<td>-220</td>
</tr>
<tr>
<td>Br⁻</td>
<td>-0.042</td>
<td>-240</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>-0.046</td>
<td>-240</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>-0.056</td>
<td>-</td>
</tr>
</tbody>
</table>

For infinite dilution, Gurney has shown that

\[
\Delta S_{\text{unit}} = \Delta S_0 - 2 R \ln M
\]

where M is the number of moles of solute per 1000 g. of solvent. (ΔS₀ refers to the ions in a hypothetical 1 molal ideal solution). Using this treatment, von Hippel and Schleich (91) have determined the partial molal ionic unitary entropies of solution for different ions. In order to do this they have, following Gurney, adopted the convention of setting the partial molal entropy of solution of the H⁺ ion equal to zero. A similar treatment has been performed by Frank and Evans (56) in order to calculate a "structure breaking entropy" \( \Delta S_{\text{St}} \), referring to an ion's effect on water structure. Three calculable entropy losses, due to

(a) formation of a firmly held hydration sheath of H₂O's around an ion,
(b) reduction of free volume when an ion enters the solution
(c) and the contribution due to partial orientation of water
molecules beyond the first layer,

are subtracted from the experimental entropies of solution, yielding
the \( \Delta S_{\text{st}} \) value. The values obtained by these two groups of workers
are tabulated in Table 2.2. A negative value of \( \Delta S \) unit or \( \Delta S_{\text{st}} \) reflects
an increase in the water structure surrounding the relevant ions whereas
a positive value indicates disruption of structure. The excellent corr-
relation between the B coefficient and ionic entropy is shown in Figure 2.1.

**Table 2.2 Partial Molal Entropies of Ions in Water at 25°C.**

<table>
<thead>
<tr>
<th>ION</th>
<th>( \Delta S ) cal deg (^{-1}) mole (^{-1}) (Ref. 56)</th>
<th>PARTIAL MOLAL UNITARY ENTROPY ( \Delta S ) unit . EU (Ref. 91)</th>
<th>&quot;STRUCTURE BREAKING&quot; ENTROPY ( \Delta S_{\text{st}} ) cal deg (^{-1}) mole (^{-1}) (Ref. 56)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(^+)</td>
<td>-39.6</td>
<td>-4.6</td>
<td>-1.1</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>-33.9</td>
<td>+6.4</td>
<td>+4.0</td>
</tr>
<tr>
<td>K(^+)</td>
<td>-25.3</td>
<td>+16.5</td>
<td>+12.0</td>
</tr>
<tr>
<td>NH(_4^+)</td>
<td>-30.5 (-25.5)</td>
<td>+19.0</td>
<td>+11.7</td>
</tr>
<tr>
<td>Rb(^+)</td>
<td>-23.1</td>
<td>+20.7</td>
<td>+14.1</td>
</tr>
<tr>
<td>Cs(^+)</td>
<td>-21.3</td>
<td>+23.8</td>
<td>+15.7</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>-65.5</td>
<td>-21.2</td>
<td></td>
</tr>
<tr>
<td>Mg(^+)</td>
<td>-84.2</td>
<td>-36.2</td>
<td></td>
</tr>
<tr>
<td>F(^-)</td>
<td>-40.9</td>
<td>-10.3</td>
<td>-3.5</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>-26.6</td>
<td>+5.2</td>
<td>+10.2</td>
</tr>
<tr>
<td>Br(^-)</td>
<td>-22.7</td>
<td>+11.3</td>
<td>+13.9</td>
</tr>
<tr>
<td>I(^-)</td>
<td>-18.5</td>
<td>+18.1</td>
<td>+17.9</td>
</tr>
</tbody>
</table>

**Note:** 1. \( \Delta S \) = the increase in entropy in passing from the hypothetical
gas state at 1 atm to a hypothetical mole fraction of unity in
solution.
14.

**Note**: 2. The value in parentheses for $\text{NH}_4^+$ has been obtained by subtracting out the contribution due to restricted rotation in the dissolved state. Frank & Evans (56) maintain that this is necessary so that comparison can be made with monatomic ions and they have estimated this quantity to be 10 e. u.

**FIGURE 2.1**

Viscosity B coefficients plotted against partial molal entropies (from reference (90), Ch. 10; on scale -5.5 for $\text{H}^+$)

**Note**: Ions with greatest ionic entropies are those with negative B coefficients from viscosity measurements.

A simple model of ionic hydration (89) predicts that cations should mainly affect the bending mode of water molecules $V_2$ while
anions should influence the stretching modes $\nabla_{1,3}$ ($\nabla_{1,3}$ is the average of symmetric $\nabla_1$, asymmetric $\nabla_3$ frequencies). The change in half band width $\Delta W_{1/2}$ is the most revealing feature for cations, an increase corresponding to structural ordering and a decrease to disordering. Structure making anions decrease $\nabla_{1,3}$ whilst structure breaking anions increase the frequency of $\nabla_{1,3}$ (see Table 2.3).

**TABLE 2.3** INFLUENCE OF SALTS ON THEIR BENDING MODE $\nabla_{2'}$ AND STRETCHING MODE $\nabla_{1,3}$ OF WATER AT 25°C. (from Ref. 89).

<table>
<thead>
<tr>
<th>SALT</th>
<th>$\Delta \nabla_{2} \text{cm}^{-1}$</th>
<th>$\Delta W_{1/2}$</th>
<th>SALT</th>
<th>$\Delta \nabla_{1,3} \text{cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeCl$_3$</td>
<td>-14</td>
<td>inc.</td>
<td>KOH</td>
<td>-5</td>
</tr>
<tr>
<td>AlCl$_3$</td>
<td>-11</td>
<td>inc.</td>
<td>KCl</td>
<td>0</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>-5</td>
<td>inc.</td>
<td>KBr</td>
<td>+12</td>
</tr>
<tr>
<td>LiCl</td>
<td>-5</td>
<td>nil</td>
<td>KI</td>
<td>+17</td>
</tr>
<tr>
<td>NaCl</td>
<td>-3</td>
<td>dec.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>-3</td>
<td>dec.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RbCl</td>
<td>-3</td>
<td>dec.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsCl</td>
<td>-3</td>
<td>dec.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: In concentrated salt solutions (12 to 1 mole ratio) an infra-red study by Choppin and Buijs (95) has established that K$^+$ is a very strong structure breaker, and Na$^+$ is a structure breaker also, in contrast to assessments of more dilute solutions.

The evaluation of ions as structure makers and breakers is certainly not restricted solely to the techniques mentioned above, though these illustrate the general features rather well. Additional information may be obtained from NMR measurements in electrolyte solutions (92, 93), X-ray diffraction, dielectric constant and partial molal heat capacity studies (77). In passing one may note that Hindman (92), on the basis of NMR studies, finds that the order of structure making for the alkali metal...
chlorides is LiCl > CsCl > RbCl > KCl > NaCl, a sequence which is in contrast to that obtained from Tables 2.1, 2.2 and 2.3 above.

Although the above discussion of structure making and breaking refers to the structure of bulk water it is also highly likely that similar, if not precisely the same, effects are observed in interfacial water. The importance of this point is amplified in later sections.

2. MONOLAYER PROPERTIES

The thermodynamic properties of liquid surfaces are well characterized (66 - 73) and will not be covered here, though the Gibbs Equation and its application to monolayer/air/water systems is examined in Chapter 5 and in Appendices I, II and III.

(a) General Introduction

Insoluble monolayers are formed from compounds containing a hydrophobic chain and a hydrophilic head group. They may be spread on a clean water surface either by dissolution from the bulk phase or by using a volatile, high purity water insoluble solvent which evaporates, leaving behind the insoluble monolayer as a residue. In 1917 Langmuir (97) found that monolayers of a variety of fatty acids of differing chain lengths reached the same limiting area per molecule on compression, indicating that the different acids all formed films with the same molecular orientation at the surface i.e. the polar, hydrophilic part of a monolayer molecule is immersed in the water, the remainder being oriented out of the water.

In these monomolecular films, essentially all the molecules are concentrated in one molecular layer at the interface and thus the
surface concentrations can be evaluated directly from the amount of material spread and the area of the surface available. Variations of size, shape etc. of the molecules can be readily examined. Monolayers can exist in different two dimensional physical states depending on the size of the lateral adhesive forces between the molecules. This is analogous to the physical properties of a three dimensional gas.

The monolayer exerts a two dimensional surface pressure \( \Pi \) (dyne cm\(^{-1}\)) which is the reduction in surface tension of the pure liquid surface by the monolayer

\[
\Pi = \gamma_o - \gamma
\]

where \( \gamma_o \) is the surface tension of the clean surface and \( \gamma \) the tension of the film or monolayer covered surface. The variation of \( \Pi \) with area available to the monolayer is generally represented by a pressure-area \( (\Pi - A) \) isotherm; compression of a three dimensional gas is analogously represented by a P-V isotherm. Consider the case of stearic acid (\( \text{C}_{17}\text{H}_{35}\text{COOH} \)) at 25° C, illustrated in Figure 2.2 below.

A feature which is normally taken as characteristic of the molecules forming the monolayer is the limiting area per molecule, \( A_o \), which is found by extrapolating the "solid", linear region of the \( \Pi - A \) curve back to the zero pressure axis. The area is normally expressed in Å\(^2\) per molecule and the surface pressure in dyne cm\(^{-1}\).

According to the nature of the head group and the pH of the substrate on which the monolayer is spread, the head group may be ionized or unionized. Alteration of \( \Pi - A \) isotherms may also arise when certain electrolytes are present in the aqueous substrate, depending markedly on the particular monolayer involved (24, 71). This point is illustrated in later sections.
(b) **Equilbrium Spreading Pressure**

If crystals (or droplets in the case of a liquid) of an insoluble amphipathic molecule are placed on a water surface, a monomolecular film is spontaneously generated, the total surface energy thereby being minimized, provided the temperature is above a certain value. If sufficient material is present, spreading will continue until the monolayer thus formed is in equilibrium with the stable bulk phase, under the prevailing experimental conditions. The surface pressure arising from this spreading process is defined as the equilibrium spreading pressure (ESP, $\Pi e$), characteristic of a particular material and
dependent only on temperature. It depends on the balance between forces favouring monolayer formation and those tending to keep the molecules within the crystal (or droplet). The thermodynamics of the spreading process have been well investigated (26, 98, 99, 100) and are not discussed here.

Spreading occurs exclusively at the air/water/solid interface (i.e. the triple interface) and the rate is proportional to the crystal perimeter (98). Roylance and Jones (30) have confirmed this fact, finding that a large crystal of hexadecanol, kept submerged in flowing distilled water, was unaffected over a period of fifteen days. If kept at the triple interface, the crystal would have entirely dissolved in a much shorter period. Furthermore those workers have demonstrated that film generation takes place from the actual crystal lattice and not from active sites. Stewart (28) has indicated that the spreading rate depends on which crystal face is exposed.

Hence an ESP may be defined as

\[ \Pi e = \gamma_o - \gamma_e \], where \( \gamma_o \) is the surface tension of a clean aqueous surface and \( \gamma_e \) is the surface tension of an aqueous surface covered by an insoluble monolayer in equilibrium with the bulk phase (crystal or droplet). The surface tension is reduced to a point where the change in surface free energy of the system is zero and spreading ceases i.e. \( \Pi e \) is reached.

(c) The structuring of water by monolayers

The fact that monolayers "structure" or "organize" the underlying water is shown by a number of experimental techniques (101). Schulman and Teorell (102) demonstrated that when an oleic acid film was moved across a water surface, a layer of water approximately \( 3 \times 10^{-3} \) cm thick was carried along with the monolayer. Blank and
La Mer (103) have shown that a monolayer consisting of an equimolar mixture of ethyl palmitate and cyclohexyl myristate, moving through a surface pressure gradient, carries with it a thick layer of subphase. Moreover this flow of film plus underlying water occurs even against a bulk flow of water. The mechanism of this process has been extensively investigated from the point of view of the geometry of the flow process and of the flow properties of the films (104, 105).

The presence of a highly organized form of water underlying a monolayer must necessarily be accounted for when considering the effects of added inorganic salts on the monolayer characteristics.

(d) Equations of State

Various authors have attempted to derive equations of state for monolayers with only very limited success (see Chapter 5). The approaches vary from the statistical mechanical to the semi-empirical and a few examples illustrate the ideas involved.

Fowler (106) considers the monolayer to behave as an ideal, two dimensional gas and neglects both the cross sections of the adsorbed molecules and the forces between them. He postulates that there is some point in the adsorbed molecule (e.g. the centre of mass) which is rigidly bound to the geometric surface of the liquid, but with a complete absence of any binding forces in the two directions in the surface. The following expression is arrived at:

$$ A = N k T - \frac{N^2 \Pi k T}{A} \int_{0}^{\infty} (e^{-E(r)/kT} - 1) r \, dr $$

where $E(r)$ is the potential energy of a pair of molecules distant $r$ apart, $N$ is the number of adsorbed molecules and $A$ is the area available to them. This equation shows reasonable agreement with experimental values at very low pressure values but is totally inadequate over a wider pressure range.
Smith (107) has developed an equation based on the CH$_2$ groups acting as a vertical stack of hard discs.

\[ \Pi + \frac{\Pi E m^2}{4A^2} \left( A \left( 1 - \frac{d^2}{4A} \right)^2 \right) = kT \]

where $E$ is a potential energy term dealing with interaction between discs, $d$ is the chain diameter and $A$ is the area occupied. This equation applies to the two dimensional liquid region only and predicts $\Pi$, $A$ and the number of carbon atoms in the chain to about 15% accuracy. Jura and Harkins (108) have integrated empirical expressions for compressibility and arrived at an equation which applies to the liquid state i.e.

\[ \Pi = C + \alpha A - b \ln A \]

where $c, \alpha$ and $b$ are variable parameters changing with temperature and chain length. On the other hand Hedge (109) has used an approach based on the van der Waal's equation for perfect gases

\[ (\Pi + a/A^2) (A - A_0) = kT \]

where $a, A_0$ are constants.

These attempts at a reproduction of $\Pi$-$A$ isotherms are all of limited application and do not give an accurate account of the monolayer state in all phases of compression. The reasons behind this, together with further equations and specific examples, are discussed in Chapter 5.

(e) **Comparison with Biological Systems**

An understanding of the characteristics of monolayer systems may help to elucidate some of the problems involved in determining the properties of cell membranes in living organisms. To date the most satisfactory concept of the cell membrane is based on the model proposed by Danielli, Davson and Harvey in 1935 (110, 111). A cell membrane is composed of lipid and protein, the lipid phase consisting of a bimolecular leaflet with the polar head groups facing outward and the lipophilic chains in the interior. Proteins are believed to be adsorbed on to the leaflet at both faces in extended conformations. The general nature of this model has been confirmed by electron microscopy (113).
The broad outline of membrane structure is fairly well known, however the functions and operational mechanisms associated with the membrane are poorly understood. For example the idea of a cell membrane acting as a simple diffusion medium does not explain the rates at which material is transported through it. The concepts of facilitated diffusion, in which flow in the direction of normal diffusion gradients is increased and of active transport, involving a net flow of some species (e.g. Na\(^+\) or K\(^+\)) against a concentration gradient, have been invoked to account for observed rates (112, 113). The physiological behaviour of cells is changed markedly by an alteration of the ionic composition of the cellular environment. Cell surfaces at normal physiological pH values carry a net negative charge of about one electronic charge per 1000 Å, which is reduced on addition of bivalent cations. For normal behaviour it is necessary to have a certain fraction of cell surface anions neutralized by Na\(^+\) and another fraction in combination with Ca\(^{2+}\), hence displacement of these ions from the cell surface will be toxic (113). The major barrier to diffusion of ions between the exterior of a nerve and its interior is the thin surface membrane. The membrane
is preferentially permeable to $K^+$ ions and develops a potential, called
the resting potential, across its surface. Stimulation of the nerve
results in the membrane becoming permeable to other ions. $Na^+$ ions
enter the nerve fibre, and $K^+$ leave, during the conduction of a nerve
impulse. During recovery (i.e. after the impulse has passed) the
original gradients of $K^+$ and $Na^+$ are restored across the plasma mem-
brane (113), the transport mechanism being only partly understood.

To explain these transport phenomena and other processes,
various models of membrane structure and function have been proposed,
involving salt migration through specific binding sites (114), carrier
molecules (115) and transformations within the membrane itself (116).
None of these has been subjected to a rigorous thermodynamic analysis
and little progress beyond the simple Danielli-Davson model has been
made. (Note: the concentration of $Na^+$ outside and the concentration
of $K^+$ inside mammalian cell membranes is about 0.15 molar).

The lipid components of a cell membrane include phospholipids,
sterols and glycerides of long chain fatty acids, all of which are known
to form insoluble monolayers. The function of biological membranes is
obviously related to molecular orientation in the layer structures, thus
a study of the surface properties of these components, or their simpler
analogues (e.g. n-octadecanol), by the monolayer approach can provide
valuable information regarding cell structure. This is particularly evident
when one realizes that the ionic composition and pH of the substrate, together
with temperature, can be kept at physiological values or altered as desired.
3.1 Pressure-Area Determinations

The pressure-area isotherms were determined using a Langmuir Trough, which is a highly developed and well established experimental technique (117, 118, 119). The trough itself was constructed from an aluminium block and its interior was coated with Teflon. It was fully automated and a diagram of the experimental arrangement is shown in Figure 3.1. Two machined Perspex rods encased in Teflon sheet were initially used as barriers, but were subsequently replaced by ones constructed from solid Teflon, designed so as to further reduce leakage of film past the barriers at high surface pressures. A stainless steel metre rule was attached to the side of the trough in order to ascertain the distance between the barriers, one of which was kept fixed in position whilst the other was moved at a constant rate with an external drive. Thus the area between the barriers could be altered at will.

The movable barrier was supported by a steel beam, attached via a nylon sleeve to a brass shaft which in turn was coupled to the gearbox of an electric motor. Initial vibration difficulties were experienced (causing larger areas per molecule, due to surface waves), however these were overcome by isolating the actual trough from its support frame by a rubber seal, using rubber mounts between the trough legs and cabinet base and incorporating an almost vibration free motor in the experimental arrangement.

The Wilhelmy plate technique (24) was used to continuously monitor the surface pressure. This involved the detection of surface
tension changes with a mica plate which was partially immersed in the substrate being studied. Changes in surface tension result in an alteration in the vertical force tending to pull the plate into the substrate and, since the mica plate was attached to a strain gauge transducer (Shinkoh Comm. Ind. Ltd.), the signal produced was registered on a one millivolt "Rika Denki" recorder. Since the strain gauge in general had an initial signal which could not be zeroed by the recorder, a small "backing off" potential, opposed to the strain gauge signal, was used to accomplish this. A 4 volt Zener diode stabilized power supply activated the transducer and shielded cables minimized any electrical interference. The trough and strain gauge were completely enclosed in a thermostated cabinet with the motor and recording equipment on the outside. Thermostating was achieved by passing water at constant temperature through coiled metal tubes which were situated in the hollow base of the Langmuir Trough and in the roof of the cabinet. Experiments were performed at 21°C and the temperature variation in the trough was no more than 0.5°C. Surface pressure values were determined from the recorder traces by calibrating the strain gauge with known masses. The chart movement (4.000 cm min^{-1}) was correlated with the barrier movement (4.173 \pm 0.002 cm min^{-1}) and hence a knowledge of the area per molecule could be obtained. The rate of reduction of area per molecule was approximately 3 A per molecule per minute.

N-octadecanol was used exclusively in this investigation to form the insoluble monolayers. Spectroscopic grade hexane was used to dissolve the n-octadecanol and it was introduced on to the water surface between the barriers with a highly accurate Agla micrometer syringe (note: the actual amount of n-C_{18}OH on the surface for each individual \Pi-A determination was about 0.1 mg.) A few minutes were allowed to elapse before commencing a run, in order that the hexane could evaporate.
FIGURE 3.1
DIAGRAM OF THE
LANGMUIR TROUGH

Barriers shown at starting position

CABINET
CABINET THERMOSTAT COILS

4 volt Strain Gauge Power Supply
Strain Gauge Output (to Recorder)
Thermostat Bath

To Motor
Drive Shaft
Levelling Screw

Rubber Mount
Nylon Sleeve

Water Surface
(Trough 1 cm deep)

Teflon Barrier
Mica Plate
(approx. 10 cm long)

Strain Gauge
Support Bracket

Thermostat Tubes

To Thermostat Bath

DOORS ENCLOSING FRONT OF CABINET NOT SHOWN
N-hexane is a good solvent for octadecanol and there is essentially complete evaporation of the n-hexane from the water surface (24). The samples were made up in 10 cc. standard flasks (with ground glass stoppers) immediately before use, in order to minimize evaporation losses.

It should be noted that all glass vessels were thoroughly steamed before use, in order to leach any adsorbed ions from the surface. The mica plate was cleaned with conductivity water and n-hexane or nitric acid between individual Π-A determinations. A flamed platinum rod was used to introduce the mica plate into the substrate, the plate being connected to the transducer by a flamed platinum wire. The salt solutions were brought to constant temperature (i.e. 21°C) in a separate water bath before they were examined in the trough. Considerable care was taken to ensure that the water or solution surface was clean by repeatedly spreading a monolayer and skimming the surface with the barriers prior to a Π-A determination, thus removing any accumulated surface active agents. So as to finally ascertain that surface active impurities were absent, the area between the barriers was reduced from greater than 700 cm² to about 25 cm² and a surface pressure of less than 0.3 dyne cm⁻¹ was taken to indicate a clean surface.

3.2 Reagent Purity

The n-octadecanol (C. Michel & Co. N. Y., U. S. A.) sample used in this investigation was of ultra-high purity and has previously been described (120, 121). Its quality was established by chromatography and by the more sensitive monolayer permeability technique of La Mer et al (122). The solid n-octadecanol crystals were relatively large and flaky in appearance; the solid can exist in three forms (123), the
stable form of which is known as the $\beta$ form. The other two forms, when they occur, gradually transform to the $\beta$ form, which is normally obtained directly on crystallization from a solvent. Since this particular sample was originally crystallized from a solvent it is in the stable $\beta$ form.

The water used throughout the investigation was triply distilled, the second stage being from alkaline permanganate. Its conductivity was generally about $10^{-6}$ ohm$^{-1}$ cm$^{-1}$ with a surface tension at $21^\circ$C of $72.6 \pm 1$ dyne cm$^{-1}$. The inorganic salts used were obtained in the following degrees of purity:

<table>
<thead>
<tr>
<th>Salt</th>
<th>Purity</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>99%</td>
<td>B.D.H.</td>
</tr>
<tr>
<td>NaCl</td>
<td>Analar Grade</td>
<td>B.D.H.</td>
</tr>
<tr>
<td>KCl</td>
<td>Analar Grade</td>
<td>B.D.H.</td>
</tr>
<tr>
<td>RbCl</td>
<td>99%</td>
<td>Schuchardt</td>
</tr>
<tr>
<td>CsCl</td>
<td>Analar Grade</td>
<td>B.D.H.</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>Analar Grade</td>
<td>B.D.H.</td>
</tr>
<tr>
<td>(CH$_3$)$_4$NCl</td>
<td>99%</td>
<td>Schuchardt</td>
</tr>
<tr>
<td>MgCl$_2$.6H$_2$O</td>
<td>Analar Grade</td>
<td>Univar</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>Analar Grade</td>
<td>B.D.H.</td>
</tr>
</tbody>
</table>

With the concentrated solutions made up from these salts it was discovered that very small amounts of highly surface active impurities caused large values of $\Pi$ in the "liquid" region of the pressure area isotherms. This was accompanied by greater discordancy between successive $\Pi-A$ isotherms than would be expected simply on the grounds of experimental error. The effect still appeared in spite of repeated skimming of the water surface in the trough and zero pressure values being recorded during a blank run (no monolayer). It was thought to be due to some form of complexing with the n-octadecanol monolayer.
and necessitated further purification of the inorganic salts. Hence NaCl, KCl, RbCl, CsCl and CaCl₂ were recrystallized out of conductivity water, dried at the pump, and, contained in an aluminium tray, were baked at 300°C in a muffle furnace for more than 12 hours. LiCl, MgCl₂, NH₄Cl and (CH₃)₄NCl were similarly recrystallized, dried at the pump and made up into a very concentrated solution. Each of these was then analysed for chloride ion (Australian Microanalytical Service) and subsequently diluted to the required concentration. The disappearance of the anomalous effect observed above, shown by a decrease in \( \Pi \) in the \( \Pi - A \) curves together with better reproducibility, indicated the removal of the impurities. These ultra high purity reagents were subsequently used in all the experimental work.

3.3. Equilibrium Spreading Pressures

A high sensitivity EMB-1 microbalance with a maximum range of 200 mg was used for measuring the ESP of n-octadecanol on water and on substrates containing various amounts of KCl. A diagram of the experimental apparatus is shown in Figure 3.2. A wire with a hook at one end and a jewelled pivot at the other was attached to one arm of the microbalance, and a mica or platinum plate was suspended from the hook. The plate, whose size was such as to incorporate the full range of the microbalance, dipped into the substrate which was contained in a shallow glass dish approximately 1 cm deep and 7.5 cm in diameter (i.e. the Wilhelmy plate technique was used again). Although there was no detectable difference in the \( \Pi_0 \) for n-octadecanol in an uncoated glass container compared with a Teflon coated one, the latter was used for all measurements as a precaution against SiO₂ etc. dissolving from the glass.
FIGURE 3-2
DIAGRAM OF EMB-1 MICROBALANCE AS USED FOR ESP MEASUREMENTS

BALANCE CASE
PACKED TUBING AND WOOL: THERMOSTAT

25 cm
24 cm
18 cm

Balance Arm Support

Balance Arm

Counter Balance

Pan

Jewelled Pivot

Alcohol Crystals

Platinum Plate (approx 2 cm long)

Water Surface

Platinum Mesh Cylinder

Teflon Coated Glass Dish, (1 cm deep 7.5 cm diameter)

MICROBALANCE CONTROL UNIT AND DOOR TO BALANCE CASE NOT SHOWN
Solid n-octadecanol crystals, after being broken up into small pieces with sharp tweezers, were placed on the surface and the increase in $\Pi$, as the molecules dissolved from the bulk phase to form a monolayer, was followed by feeding the microbalance output into a "Rika Denki" recorder. (Note: the crystals were not ground to a powder, since this may induce a phase change, altering the spreading characteristics - see later sections). Due to slight convection currents the flakes of solid alcohol tended to move about on the substrate surface. Unfortunately some flakes would become attached to the plate, altering its effective perimeter and causing incorrect surface pressure values to be registered. To avoid this difficulty the alcohol crystals were constrained within the confines of a flamed platinum mesh cylinder (about 1.5 cm in diameter), which protruded above the liquid surface.

The microbalance, being very compact, was easily thermostated by passing water through plastic tubing tightly wound around its outer case. A thick layer of wool was then packed around the tubing so as to complete the insulation. The interior cabinet temperature was kept at $21^\circ C$ and during the course of an ESP run, which was in general of about 24 hours duration, varied by no more than $\pm 0.4^\circ C$. All solutions were thermostated at $21^\circ C$ prior to placing them in the microbalance. Monolayers were introduced on to the surface and swept off before the crystals were spread, ensuring a clean liquid surface. The solution temperature was checked when an ESP was reached and was compared with the cabinet temperature, identical values generally being obtained.

With mica plates and substrates containing potassium chloride inconsistent results were evident. Blank runs (i.e. without alcohol) showed a gradual (over a period of some hours) increase in the weight
of the mica plate, due to epitaxing of KCl on to the mica surface, and therefore decreasing $\Pi$. With platinum plates this process does not occur, thus for all substrates containing KCl a flamed platinum plate was used in the ESP measurements.

The alcohol crystals could easily be recovered after an ESP determination, washed and dried. Used again, the effect of prolonged exposure to the substrate and the possibility of hydrate formation could be considered (see later sections).

### 3.4 Surface Tension Measurements

Except for some slight variations, the experimental arrangement was identical to that used in the ESP measurements. Since the plate is only dipping into the substrate for a short period (i.e. several minutes at most) during a surface tension measurement, the problem of KCl epitaxing on to mica is not important, however both mica and platinum plates were used for the surface tension measurements as a means of comparison. The microbalance had a maximum load which it could support and this limited the amount of counterbalancing which could be carried out. Since mica is very light, larger plates (greater accuracy) could be used than for platinum, the factor controlling plate size being the maximum load capacity of the microbalance.

Great care was taken to ensure that the plate was thoroughly wetted (i.e. contact angle = 0), the plates being thoroughly cleaned between readings. At the same time it was necessary to avoid the presence of liquid droplets on the plate above the contact line, since these take some time to evaporate and/or drain off. Readings were generally taken 30 seconds to 1 minute after introducing the plate into the substrate. Again all solutions were thermostated at $21^\circ$C prior to
use and the solution surface was cleaned beforehand as for the ESP measurements. In general very little variation was found between measurements where the surface was cleaned and those where it was not. The solution and cabinet temperatures were measured before and after a set of readings, the variation being no more than $\pm 0.2^\circ C$. 
CHAPTER 4. RESULTS

4.1 The $\Pi$-A isotherms for n-octadecanol on various substrates at 21°C.

Figures 4.1 to 4.5 and Table 4.1 summarise the effect of various inorganic salts on the pressure-area isotherms of n-octadecanol at 21°C. No pH control was necessary as alcohol monolayers are unaffected by pH changes between 2 and 10 (24) and the solutions used here were slightly acid due to the presence of dissolved CO$_2$$. The $\Pi$-A isotherm of n-C$_{18}$OH on water was used as a standard on all occasions and compares very favourably with those in the literature (24). It represents the average of at least 50 separate determinations and yields a limiting area per molecule of $20.1 \pm 0.1 \text{Å}^2$ at 21°C.

In determining the isotherms on substrates containing a salt, the following procedure was adopted. Firstly, using triply distilled water as the substrate, 2 or 3 isotherms were obtained. Then the Langmuir trough was emptied and, after filling with salt solution, a sequence of 6 to 8 isotherms was determined. Finally, to ensure that there was no contamination introduced with the alcohol sample, conductivity water or the apparatus itself, an additional 2 or 3 standard isotherms on triply distilled water were again obtained. Satisfactory agreement between both sets of standards ensured that the results for the salt solutions could be used with confidence, since this technique provided an excellent method of checking reproducibility. The recorder traces for the individual runs on a particular substrate were superimposed and the raw data from their mean could be simply expressed in terms of surface pressure and area per molecule, since the amount of alcohol spread per unit area on a surface was known. In addition to the experiments above, certain specific tests itemized below were performed.
(a) In order to detect whether aluminium, dissolving from the trough base and entering into solution through pitholes in the Teflon coating might affect the $\Pi$-A results, small quantities of aluminium chloride (about 0.1 g) were intentionally added to several substrates (water only and water + salt). No effect on the compression characteristics of n-octadecanol monolayers was observed.

(b) Blank runs (i.e. in the absence of a monolayer) were performed on KCl containing substrates so as to ascertain whether or not salt had any effect on the mica plate. Throughout the duration of a normal $\Pi$-A run there was no detectable alteration of $\Pi$ due to the action of salt. These blank runs also demonstrated that there were no surface active impurities introduced by the salt.

(c) Leakage of the monolayer past the barriers is a problem which is inherent in all monolayer work where Langmuir type troughs are involved. In order to detect the amount of leakage, if any, compression of the monolayer was halted at various areas and the pressure was monitored continuously for a period of from 3 to 5 minutes. Up to about 20 dyne cm$^{-1}$ there was no detectable leakage. At higher pressures (about 35 dyne cm$^{-1}$) leakage was appreciable. Since the monolayer is by this stage in the "solid" region of the isotherm, the only effect this has is to slightly decrease the slope $\frac{d\Pi}{dA}$.

The $\Pi$-A isotherms on the various salt solutions show the following features :-

1. For the 4 molar chlorides the monolayer is expanded in the "liquid" region and the expansion is in the order: $\text{MgCl}_2 \gg \text{CaCl}_2 \gg \text{LiCl} \gg \text{NaCl} \gg \text{KCl} \gg \text{RbCl} \simeq \text{NH}_4 \text{Cl} \gg \text{CsCl}_2 \simeq \left(\text{CH}_3\right)_4\text{N}^+\text{Cl}^{-}$. 
The gradients in the "solid" region differ from that of pure water, an effect which is possibly due to leakage as mentioned in (c) above. Moreover the standard $\Pi$-A isotherm on water represents an average of a far larger sample of individual isotherms than for the salt solutions, a point which may also account for this fact. The limiting areas are unaffected as shown in Table 4.1, indicating that the presence of inorganic salts has no influence on the packing of the head groups. Additional comments on these features are made in 5.3.

2. A decrease in salt concentration causes a contraction of the monolayer, as shown for KCl in Figure 4.3. For the sake of clarity the 1, 2.5, 3 and 3.5 molar KCl isotherms are not shown here, however data obtained from them is illustrated in Figures 4.7 to 4.11 and tabulated in Appendix V. The 0.01 molar KCl isotherm coincides with that obtained for pure water.

Errors :-

The nature of the precision equipment used in delivering a solution of the alcohol on to the substrate surface, combined with the experimental technique of making up solutions just prior to using them, results in small errors in ascertaining areas per molecule. Evidence for this is provided in Table 4.1 where the limiting areas generally have a mean deviation of $\pm 0.2\text{A}^2$ or better, this error range having been obtained from six or more separate values.

Errors in the $\Pi$ values occur due to cutting, aligning and calibrating the mica plate, recorder reproducibility, and to the introduction of minute amounts of surface active impurities into the system, despite stringent cleaning procedures. The first two of these total no more than 1% of the surface pressure, the last cannot be estimated. The $\Pi$-A isotherms for the various salt solutions are the average of a minimum
of at least six separate determinations. In certain cases many more than six have been used, e.g. water and the KCl solutions. Generally the isotherms are reproducible to no better than $-0.5$ dyne cm$^{-1}$, this value being an average range encompassing the various $\Pi$ values obtained from the separate determinations.

\begin{table}
\centering
\caption{Limiting areas for n-octadecanol on various salt solutions at 21$^\circ$C.}
\begin{tabular}{lll}
Substrate & Limiting area, A$^2$ & Substrate & Lim A; A$^2$
\hline
triply distilled water & 20.1$^+$.1 & 4M LiCl & 20.0$^+$.1 \\
4M KCl & 20.1$^+$.2 & 4M NaCl & 19.9$^+$.2 \\
3.5M KCl & 20.0$^+$.2 & 4M RbCl & 20.0$^+$.2 \\
3M KCl & 20.1$^+$.1 & 4M CsCl & 20.0$^+$.2 \\
2.5M KCl & 20.1$^+$.3 & 4M NH$_4$Cl & 20.0$^+$.1 \\
2.0M KCl & 20.2$^+$.1 & 4M (CH$_3$)$_4$N$^+$Cl$^-$ & 20.1$^+$.4 \\
1.0M KCl & 20.1$^+$.2 & 4M MgCl$_2$ & 19.8$^+$.2 \\
0.01M KCl & 20.1$^+$.1 & 4M CaCl$_2$ & 19.9$^+$.2 \\
\end{tabular}
\end{table}

4.2 (a) Equilibrium Spreading Pressures.
(b) The Surface Tension of Salt Solutions.

(a) Figure 4.6 and Table 4.2 reveal the ESP results obtained for n-octadecanol on substrates containing KCl of varying concentrations. The increase in ESP with KCl appears to be linear and a least squares analysis performed on the data yielded the straight line shown in Figure 4.6. Each $\Pi$ value represents the average of seven or more isolated determinations and the error ranges shown are expressed as mean deviations. Maximum estimable errors involving the Wilhelmy plate techniques, recorder reproducibility and temperature fluctuations are small compared to these (i.e. less than 0.5% of each $\Pi$ value).
TABLE 4.2  Equilibrium Spreading Pressures of n-C_{18}OH on KCl solutions at 21°

<table>
<thead>
<tr>
<th>KCl concentration, moles 1^{-1}</th>
<th>ESP, dyne cm^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>38.4 ± 0.5</td>
</tr>
<tr>
<td>3</td>
<td>36.5 ± 0.5</td>
</tr>
<tr>
<td>2</td>
<td>35.6 ± 0.6</td>
</tr>
<tr>
<td>1</td>
<td>34.2 ± 0.3</td>
</tr>
<tr>
<td>0 (triply distilled water)</td>
<td>32.1 ± 0.1</td>
</tr>
</tbody>
</table>

A sample ESP curve is included below for reference.

FIGURE 4.12
ESP - time curve for n-octadecanol on 4M KCl.

It shows 3 distinct regions (a, b and c). Firstly there is a relatively short induction period during which the release of alcohol molecules
from the solid \( \beta \) form is slow. This is followed by a fairly rapid increase in \( \Pi \) to about 30 dynes cm\(^{-1} \) and finally the ESP curve levels off at the limiting \( \Pi_e \) value, showing no decrease in \( \Pi \) with time. Brooks and Alexander (26) ascribe this latter feature (i.e. the drop in \( \Pi \) with time) to impurities in their alcohol samples. The existence of the three regions mentioned above is similar to that obtained by Roylance and Jones for their ESP determinations of hexadecanol and by La Mer and Healy (129) for their ESP determinations of the various crystal forms of hexadecanol and octadecanol.

In these spreading experiments with octadecanol, certain specific measurements other than those mentioned above were performed.

(i) The ESP of \( n \)-octadecanol was measured with a platinum plate and with a mica plate. There was no appreciable difference in the ESP's obtained and some sample results are included below.

<table>
<thead>
<tr>
<th>plate type</th>
<th>ESP at 21(^\circ)C, dyne cm(^{-1} ) (pure water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mica</td>
<td>32.3, 32.0</td>
</tr>
<tr>
<td>Platinum</td>
<td>32.1, 32.2</td>
</tr>
</tbody>
</table>

(ii) In order to determine the effect of exposure to concentrated salt solutions and possible alcohol hydrate formation on the attainment of ESP's, crystals of alcohol were recovered from individual determinations. After washing and drying at the pump and on filter paper, they were again used for ESP measurements. Within the limits of experimental error, there was no detectable difference between used and fresh crystals, e.g. crystals which had been exposed to both salt and water produced an ESP of 32.0 dyne cm\(^{-1} \) for a pure water substrate.

(iii) As mentioned in 3.3, the solid alcohol crystals were broken up with tweezers and not powdered with a mortar and pestle. When the crystals were ground, higher \( \Pi_e \) values were recorded (e.g. values of
35.4, 32.6 and 35.2 dyne cm\(^{-1}\) were measured in preliminary experiments using powdered crystals at 21\(^{\circ}\)C). This point is amplified in 5.2.

(b) Figure 4.6 and Table 4.3 summarise the surface tension measurements obtained for the various salt solutions at 21\(^{\circ}\)C in the absence of a monolayer of n-octadecanol. The available literature values are also tabulated as a means of comparison. In general there is good correlation between the two, allowing for differences due to the molarity and molality scales. For instance the molality of a 2 molar KCl solution is 2.13 whilst the molality of a 4 molar solution is 4.56.

<table>
<thead>
<tr>
<th>SALT conc'n in moles l(^{-1})</th>
<th>(\gamma), dyne cm(^{-1}) (present study)</th>
<th>(\Delta\gamma) (rel H(_2)O), dyne cm(^{-1})</th>
<th>(\gamma), dyne cm(^{-1}) (from ref 51) molal conc scale for salt soln</th>
</tr>
</thead>
<tbody>
<tr>
<td>4M LiCl</td>
<td>79.6 ± 3</td>
<td>7.0 ± 4</td>
<td>79.3 ± 2</td>
</tr>
<tr>
<td>4M NaCl</td>
<td>79.3 ± 2</td>
<td>6.7 ± 3</td>
<td>79.1 ± 2</td>
</tr>
<tr>
<td>4M KCl</td>
<td>78.1 ± 2</td>
<td>5.5 ± 3</td>
<td>78.1 ± 2</td>
</tr>
<tr>
<td>3.0M KCl</td>
<td>76.7 ± 2</td>
<td>4.1 ± 3</td>
<td>76.9 ± 2</td>
</tr>
<tr>
<td>2.0M KCl</td>
<td>75.7 ± 2</td>
<td>3.1 ± 3</td>
<td>75.5 ± 2</td>
</tr>
<tr>
<td>1.0M KCl</td>
<td>74.2 ± 2</td>
<td>1.6 ± 3</td>
<td>74.2 ± 2</td>
</tr>
<tr>
<td>4M RbCl</td>
<td>77.4 ± 3</td>
<td>4.8 ± 4</td>
<td>77.4 ± 2</td>
</tr>
<tr>
<td>4M CsCl</td>
<td>76.1 ± 3</td>
<td>3.5 ± 4</td>
<td>77.4 ± 2</td>
</tr>
<tr>
<td>4M NH(_4)Cl</td>
<td>77.1 ± 3</td>
<td>4.5 ± 4</td>
<td>77.4 ± 2</td>
</tr>
<tr>
<td>4M (CH(_3))(_4)N(^+)Cl(^-)</td>
<td>76.0 ± 3</td>
<td>3.4 ± 4</td>
<td>77.4 ± 2</td>
</tr>
<tr>
<td>4M MgCl(_2)</td>
<td>90.1 ± 4</td>
<td>17.5 ± 5</td>
<td>72.59 ± 5</td>
</tr>
<tr>
<td>4M CaCl(_2)</td>
<td>88.3 ± 4</td>
<td>15.7 ± 5</td>
<td>72.59 ± 5</td>
</tr>
<tr>
<td>WATER</td>
<td>72.6 ± 1</td>
<td>0</td>
<td>72.59 ± 5</td>
</tr>
</tbody>
</table>
41.

Both platinum and mica plates have been used throughout, there being no appreciable difference in the results obtained with either type. Each value of $\bar{\gamma}$ represents the average of at least twenty separate determinations in which the substrate was replaced at least twice. For water and the KCl solutions the sample is of at least fifty distinct values with the substrate having been altered many times. The error ranges quoted are mean deviations, errors involving the plate techniques, balance reproducibility and ambient temperature again being small by comparison.

The elevation of the surface tension of water ($\Delta\gamma$) by the 4 molar salts decreases in the sequence $\text{MgCl}_2 > \text{CaCl}_2 > \text{LiCl} > \text{NaCl} > \text{KCl} > \text{RbCl}_2 > \text{NH}_4\text{Cl} > \text{CsCl} > (\text{CH}_3)_4\text{N}^+\text{Cl}^-$. This is exactly the same sequence as observed for the decreasing contraction of the n-octadecanol $\Pi - A$ isotherms.

**General Comment:**

Referring to Table 4.4 and Figure 4.6, it can be seen that the elevation of the ESP ($\Delta\Pi e$) of n-octadecanol on substrates containing KCl, compared with water alone, parallels within the limits of experimental error the elevation of the surface tension of water ($\Delta\gamma$) by KCl itself. Further recalling that $\Pi e = \gamma_0 - \gamma e$ (see 2.2(b)), it can be seen that $\gamma e$ is independent of KCl concentration.

**TABLE 4.4** The ESP increment ($\Delta\Pi e$) surface tension elevation ($\Delta\gamma$) and $\gamma e$ value for KCl solutions at 21°C.

<table>
<thead>
<tr>
<th>KCl concentration moles $1^{-1}$</th>
<th>4</th>
<th>3</th>
<th>2</th>
<th>1</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta\Pi e$, (dyne cm$^{-1}$)</td>
<td>$6.3^+ .6$</td>
<td>$4.4^+ .6$</td>
<td>$3.5^+ .7$</td>
<td>$2.1^+ .4$</td>
<td>$0$</td>
</tr>
<tr>
<td>$\Delta\gamma$, (dyne cm$^{-1}$)</td>
<td>$5.5^+ .3$</td>
<td>$4.1^+ .3$</td>
<td>$3.1^+ .3$</td>
<td>$1.6^+ .3$</td>
<td>$0$</td>
</tr>
<tr>
<td>$\gamma e$, (dyne cm$^{-1}$)</td>
<td>$39.7^+ .7$</td>
<td>$40.2^+ .7$</td>
<td>$40.1^+ .8$</td>
<td>$40.0^+ .5$</td>
<td>$40.5^+ .2$</td>
</tr>
</tbody>
</table>
4.3 The influence of an alcohol monolayer on the surface tension of solutions containing KCl.

The results mentioned in this section are analysed by two different methods in section 5.4 (see Figs. 4.7 to 4.11 and Appendix V), hence the data have been plotted in two different fashions.

Figure 4.7 represents the elevation of the surface tension of water plotted as a function of \( \log_{10}(Y^+ - C_{KCl}) \), where \( Y^+ \) is the mean ionic molar activity coefficient and \( C_{KCl} \) is the molar concentration of KCl. Since data for \( Y^+ \) at the desired KCl concentrations was not available, the values of \( Y^- \) have been obtained from \( f^- \), the mean ionic molal activity coefficient (refer Appendix V). The curve shown in Figure 4.7 has been drawn as a line of best fit. Similarly Fig. 4.9 illustrates the elevation of the surface tension of water plotted against the mole fraction of KCl. The straight line appearing here has been obtained by a least squares analysis. The error bars in both represent the mean deviations mentioned in 4.2 (b).

In Figures 4.8 (A + B), 4.10 and 4.11 the surface tension of a monolayer covered surface at 21 and 20 Å per molecule has been plotted as a function of \( \log_{10}(Y^+ - C_{KCl}) \) and also as a function of the mole fraction of KCl. In the first case the curves are drawn as lines of best fit whereas in the second a least squares analysis yielded the straight lines shown. The surface pressure data was obtained in the first instance simply by reading off the relevant \( P \) value from the \( P-A \) isotherm obtained for a given KCl concentration. Then, recalling that \( \bar{\gamma} = \gamma_o - P \), substitution of the appropriate \( \gamma_o \) value for the particular KCl concentration concerned yielded the required value of \( \bar{\gamma} \). The error bars shown in these figures include errors in both \( \gamma_o \) and \( P \). The relevant data is tabulated in Appendix V. Although not shown here, reference to Table 4.4 indicates that a plot
43.

of $\gamma$ versus $\log_{10}(Y^+ C_{KCl})$ or mole fraction of KCl would yield a horizontal line.

The gradients of the various curves mentioned above are tabulated in Table 4.5 below (at a bulk concentration of 3 moles $1^{-1}$). Calculations using these values are made in 5.4.

**TABLE 4.5**

<table>
<thead>
<tr>
<th>Conditions at 21°C.</th>
<th>$\frac{d\gamma}{d \log_{10}(Y^+ C_{KCl})}$</th>
<th>$\frac{d\gamma}{dx}$ where x = mole fraction of KCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Elevation of $H_2O$ by KCl; infinite area per molecule</td>
<td>7.5</td>
<td>86.7</td>
</tr>
<tr>
<td>2. 21 $A^2$ per molecule</td>
<td>5.0</td>
<td>49.0</td>
</tr>
<tr>
<td>3. 20 $A^2$ per molecule</td>
<td>4.0</td>
<td>44.6</td>
</tr>
<tr>
<td>4. area at ESP (ca 19.0 to 19.3 $A^2$)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

These results indicate that as the area per molecule available is reduced by compression, $\frac{d\gamma}{d \log_{10}(Y^+ C_{KCl})}$ and $\frac{d\gamma}{dx}$ both decrease until each reaches a value of zero at the area per molecule corresponding to the ESP.
PRESSURE AREA CURVES FOR N-OCTADECANOL ON VARIOUS SUBSTRATES AT 21°C.
Figure 4.2

Pressure-area curves for n-octadecanol on various substrates at 21°C.

Conductivity water
4M KCl
4M RbCl
4M CsCl
FIGURE 4.3

CONDUCTIVITY WATER

4 M KCl
2 M KCl

SURFACE PRESSURE dyne cm⁻¹

AREA PER MOLECULE Å²

PRESSURE AREA CURVES FOR N-OCTADECANOL ON VARIOUS SUBSTRATES AT 21°C.
Figure 4.4

Conductivity:
- $\text{H}_2\text{O}$
- $4\text{M} \text{NH}_4^+\text{Cl}^-$
- $4\text{M} \text{(CH}_3\text{)}_4\text{N}^+\text{Cl}^-$

Pressure area curves for N-octadecanol on various substrates at 21°C.
FIGURE 4.5

CONDUCTIVITY WATER
4M MgCl₂
4M CaCl₂

SLOW PRESSURE, dyne cm⁻¹

AREA PER MOLECULE, A²

PRESURE—AREA CURVES FOR N—OCTADECANOL ON
VARIOUS SUBSTRATES AT 21° C
FIGURE 4.6

a. PLOT OF ESP VERSUS $[\text{KCl}]$ IN AQUEOUS SUBSTRATE FOR N-C$_{18}$OH AT 21°C.

b. PLOT OF ELEVATION OF $\gamma$ OF WATER BY KCI AT 21°C.
Figure 4.7

Elevation of the surface tension of water by KCl at 21°C, shown as $\gamma$ versus $\log_{10} [Y^{\pm} \text{KCl}]$.
PLOTS OF $\gamma$ VS $\log_{10}[Y^{\pm} CKCl]$ FOR N-CH$_2$OH AT VARIOUS FIXED AREAS, 21°C

A. 20 A$^2$ per molecule

B. 21 A$^2$ per molecule
Elevation of surface tension of water, plotted as mole fraction of KCl (21°C)
FIGURE 4.10

PLOT OF $\gamma$ VS MOLE FRACTION KCl FOR C$_{18}$OH AT 21 A$^2$ (21°C)
FIGURE 4.11

PLOT OF $\gamma$ VERSUS MOLE FRACTION OF KCl FOR C$_{18}^{18}$OH AT 20 A$^2$ (21°C)

--- MOLE FRACTION OF KCl ---

MOLE FRACTION OF KCl
The topics in the first four sections of this chapter are discussed, to a large degree, in virtual isolation from one another. Overall relationships and comparisons are delayed until each topic has been covered fully.

5.1 The Surface Tension of Salt Solutions

At this stage it is useful to consider some of the basic ideas behind the concept of surface tension. It is a well-known phenomenon that a given mass of liquid will spontaneously assume a spherical shape, unless influenced by external constraints, because in this configuration minimum surface energy is achieved. Normally external conditions govern the final area assumed. This spontaneous contraction leads to the idea of a tensile stress or surface tension existing within the surface of all liquids, arising from an asymmetric distribution of the various intermolecular attractive forces. This results in a net attraction into the bulk phase in a direction normal to the surface. The development of surface tension is thus associated with interactions between molecules in the surface region (31), which is composed of a number of molecular layers (see chapter 2) and will also depend on molecular orientation within this region (e.g., as influenced by insoluble monolayers). Whether it be at a liquid/liquid, liquid/solid or liquid/air interface the surface region, as has already been noted, is one where considerable structure occurs.

It has been known for many years that inorganic salts elevate the surface tension of water (51, 52). This elevation can be contrasted with the lowering of surface tension exhibited, for instance, in the case of long chain fatty acids, a reflection of their accumulation at the interface. An anomaly known as the Jones-Ray (53) effect has been found in this
overall surface tension elevation by inorganic salts. Jones and Ray (53) made a series of measurements of the surface tension of dilute aqueous solutions of several salts, using a highly sensitive differential capillary rise method. Their results indicated an apparent decrease in surface tension with increasing salt concentration to a minimum around $2 \times 10^{-3}$ M, before rising again. This rather surprising result implied that there was positive adsorption of salt at the surface at very low concentrations, followed by the expected negative adsorption at higher concentrations. The existence of this effect has been questioned (54, 55, 130, 131) and it appears to be due to a peculiarity in the experimental technique concerned. The effective bore of the capillary changes at very low concentrations and this results in lower surface tension values than expected (54). Although Jones and Wood (131) have confirmed that the surface tension does in fact rise at these lower concentrations, at present there is still some argument about the existence of this anomaly (12, 71). However the overwhelming effect of inorganic salts is to increase the surface tension of water.

A review of recent ideas concerning the surface tension and surface potentials of aqueous electrolyte solutions is given by Randles (130). Increments in surface tension at low salt concentrations are explained on the basis of electrostatic forces, analogous to the Debye-Huckel theory for dilute solutions, and a model developed by Onsager and Samaras (133) leads to an approximate agreement between the experimental and theoretical increments in surface tension for different inorganic salts at low concentrations. However this model cannot account for the marked differences in behaviour of various salts. These differences are apparently due to specific adsorptive forces whose mechanism is unknown but which must be "... related to the structure of the hydration shell of the ions concerned and the structure of the water surface" (130). At higher concentrations the disparity between individual salts becomes even larger and there is no simple interpretation available.
57.

The concept of surface potential is admirably discussed by Parsons (72) and, apart from noting that surface potential is generally given the symbol \( \chi \), it is not considered any further here. Randles (130, 132) has measured the concentration dependence of \( (\chi_{\text{solution}} - \chi_{H_2O}) \) for aqueous solutions of various salts and finds that for the 3M solutions of LiCl, NaCl, KCl and CsCl, the surface potential increments are +13, +9, +6 and +6 mv respectively, a sequence which is comparable to that found for the surface tension increments reported in this investigation. Again Randles (132) notes that there is no satisfactory explanation of the adsorptive forces which operate on the inorganic ions concerned.

A comparison between surface tension and other physical parameters (e.g. activities, entropies of solution) may yield information relating to the mechanism of the surface tension elevation. Although data was available for KCl at 20°C and at the concentrations desired (51, 52), its surface tension was measured both as a check on technique and reagent quality. Extreme accuracy was not the aim, since this necessitates the use of a more sensitive technique, such as the capillary rise method, together with more precise temperature control. The results quoted in Table 4.3 and illustrated for KCl in Figure 4.6 as a function of concentration are sufficiently accurate to permit reliable calculations and comparisons to be made. Data from references 51 and 52 are included to illustrate this point. The increase in the surface tension of water due to the presence of dissolved inorganic salts can initially be examined from two points of view.

By means of ion-dipole interactions, solute ions have a tendency to attract surface water molecules into the bulk and additional work over that of the pure solvent must be performed against these electrostatic forces for the generation of fresh surface. Furthermore to move a dissolved
ion together with its attendant hydration sheath into the interface requires more work than that associated with a physically smaller water molecule, since the latter requires less new surface for its accommodation.

i.e. $\Delta \gamma = f$ (salt activity, ion-dipole interaction, degree of hydration).

(N.B. terms such as solution viscosity may also be included).

These quantities within the brackets are not mutually exclusive from one another and any mathematical expression will necessarily be complicated. The relationship between $\Delta \gamma$ and salt activity is illustrated in Figures 4.6, 4.7 and 4.9 for KCl whilst the dependence on charge density, related to the strength of the ion-dipole interactions, is shown for the alkali metal cations in Figure 5.1 below.

The qualitative statements above are borne out by the experimental results. From Li to Cs (and for the pairs NH$_4^+$, TMA$^+$ and Mg$^{2+}$, Ca$^{2+}$), $\Delta \gamma$ becomes smaller, showing the greater ease in moving an ion into the interface as the amount of hydration decreases. At the same time there is a decrease in charge density with decreasing $\Delta \gamma$, hence less work is required to move an ion against the smaller ion-dipole interactions.

The picture, however, is not quite so simple. Having noted that surface tension depends on molecular attraction and orientation within an ordered interfacial region, it is highly likely that structural effects also play an important role in the development of surface tension. As mentioned in Chapter 2, Frank & Evans (56) have analysed the effect of ions on the structure of water and, in considering the entropy of solution of monatomic ions in water, calculate a "structure breaking" entropy $\Delta S_{st}$, which refers directly to the ions' alteration of water structure. A similar analysis by Von Hippel and Schleich (91) has
FIGURE 5.1

PLOT OF $\Delta \gamma$ VERSUS CHARGE AREA RATIO FOR VARIOUS MONOVALENT CATIONS. [Cl$^-$ AS REFERENCE ANION]

NOTE: CRYSTALLOGRAPHIC RADII USED.
yielded another "structural entropy" term, $\overline{\Delta S}$ unitary, which also purports to measure changes in water structure. Both of these quantities are tabulated in Table 5.1 along with the surface tension increments for the various inorganic salts. Moreover activity coefficients of electrolytes in aqueous solution are significant in that they represent a measure of the total interaction of the ions with themselves and with the water. Nonideality and ion sequence effects in bulk solution should be comparable to those in the interfacial layers, since in essence these can be thought of as two dimensional aqueous solutions. Hence the available activity coefficient data for the 4 molal chlorides is shown in Table 5.2.

**TABLE 5.1** Comparison between "Structural Entropy" terms (refs. 56, 91) for various ions and the surface tension elevation of water due to dissolved 4 molar salts at $21^\circ$C.

<table>
<thead>
<tr>
<th>ION</th>
<th>$\overline{\Delta S}$ unitary EU</th>
<th>$\Delta S_{st}$ cal deg$^{-1}$ mole$^{-1}$</th>
<th>SALT</th>
<th>$\Delta \gamma$ (present dyne cm$^{-1}$ study)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
<td>-4.6</td>
<td>-1.1</td>
<td>LiCl</td>
<td>$7.0^{+0.4}$</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>+6.4</td>
<td>+4.0</td>
<td>NaCl</td>
<td>$6.7^{+0.3}$</td>
</tr>
<tr>
<td>K$^+$</td>
<td>+16.5</td>
<td>+12.0</td>
<td>KCl</td>
<td>$5.5^{+0.3}$</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>+19.0</td>
<td>+11.7</td>
<td>NH$_4$Cl</td>
<td>$4.5^{+0.4}$</td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>+20.7</td>
<td>+14.1</td>
<td>RbCl</td>
<td>$4.8^{+0.4}$</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>+23.8</td>
<td>+15.7</td>
<td>CsCl</td>
<td>$3.5^{+0.4}$</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>-36.2</td>
<td>-</td>
<td>MgCl$_2$</td>
<td>$17.5^{+0.5}$</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>-21.2</td>
<td>-</td>
<td>CaCl$_2$</td>
<td>$15.7^{+0.5}$</td>
</tr>
<tr>
<td>F$^-$</td>
<td>-10.3</td>
<td>-3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>+5.2</td>
<td>+10.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br$^-$</td>
<td>+11.3</td>
<td>+13.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I$^-$</td>
<td>+18.1</td>
<td>+17.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 5.2  Relationship between the mean molal activity coefficient at 25°C (ref 74) and the surface tension elevation of water due to dissolved 4 molar salts at 21°C.

<table>
<thead>
<tr>
<th>SALT</th>
<th>MgCl₂</th>
<th>CaCl₂</th>
<th>LiCl</th>
<th>NaCl</th>
<th>KCl</th>
<th>RbCl</th>
<th>NH₄Cl</th>
<th>CsCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>f⁺</td>
<td>5.54</td>
<td>2.93</td>
<td>1.510</td>
<td>0.792</td>
<td>0.582</td>
<td>0.541</td>
<td>0.560</td>
<td>0.474</td>
</tr>
<tr>
<td>(at 4 molal)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Δγ/dyne cm⁻¹ (present study)</td>
<td>17.5⁻⁺ 5</td>
<td>15.7⁻⁺ 5</td>
<td>7.0⁻⁺ 3</td>
<td>4.67⁻⁺ 3</td>
<td>5.5⁻⁺ 3</td>
<td>4.8⁻⁺ 4</td>
<td>4.5⁻⁺ 4</td>
<td>3.5⁻⁺ 4</td>
</tr>
</tbody>
</table>

Referring to the activity coefficient data it can be seen that

Δγ, a reflection of an interfacial phenomenon, is related to non-ideality in bulk and therefore surface behaviour i.e. interactions between solvent-solute, solute-solute, and solvent-solvent in the surface layers are related to surface tension. For the 4 molar salts examined, in general a low value of the mean activity coefficient corresponds to a low value ofΔγ. Furthermore it can be seen that structure makers such as Mg²⁺ and Li⁺ have larger activity coefficients than do structure breakers such as Cs⁺ and Rb⁺. The ΔSst and ΔS unitary data are more informative, since it can be seen that the more structure disordering the cation is (i.e. the more positive is ΔSst or ΔS unitary) the lower will be the value of Δγ. Hence Cs⁺ is probably more easily accommodated in the interface than Li⁺ due to the fact that it introduces more disorder in the structured region since there is a more favourable entropy contribution from Cs⁺ than from Li⁺. The validity of this statement is analysed in quantitative terms below. It seems certain from the above comparisons that any consideration of the surface tension elevation by salts must take account of non-ideality and structural effects in the interface.

The adsorption of potassium chloride at the air/water interface is now considered (see Table 4.3 and Figures 4.6, 4.7 and 4.9).
At constant temperature and pressure the variation of surface tension of an electrolyte solution is given by

\[ d\gamma = -\sum i i \mu_i \]  \hspace{1cm} (1)

where \( i \) is the surface concentration in moles cm\(^{-2}\) of species \( i \) and \( \mu_i \) is its chemical potential.

The system contains five principal species, \( K^+ \), \( Cl^- \), \( OH^- \), \( H^+ \) and \( H_2O \). Potassium chloride is assumed to be completely dissociated whilst \( H^+ \) and \( OH^- \) are present in very small amounts and are not independent components, since

\[ H_2O \rightleftharpoons H^+ + OH^- \]

hence,

\[ d\gamma = -\int_{H_2O} \mu \text{d}H_2O - \int K^+ \mu \text{d}K^+ - \int Cl^- \mu \text{d}Cl^- - \int H^+ \mu \text{d}H^+ - \int OH^- \mu \text{d}OH^- \]

Electroneutrality conditions for the bulk and surface are:

\[ CK^+ + CH^+ = CC1^- + COH^- \]  \hspace{1cm} (3)

and \[ \int K^+ + \int H^+ = \int Cl^- + \int OH^- \]  \hspace{1cm} (4)

where the various Ci's refer to bulk molar concentrations.

In this present study the pH was not held constant, nor was the change in pH known, hence the following assumptions must be made:

\[ \int K^+ \gg \int H^+ \text{ and } CK^+ \gg CH^+ \]

\[ \int Cl^- \gg \int OH^- \text{ and } CC1^- \gg COH^- \]

These are quite reasonable in view of the concentrated KCl solutions being studied and lead immediately to

\[ \int K^+ = \int Cl^- = KCl \]  \hspace{1cm} (5)

and \[ CK^+ = CC1^- = CKCl \]  \hspace{1cm} (6)
where $\int KCl$ and $C_{KC1}$ are the total stoichiometric adsorption and the stoichiometric concentration of KCl.

The assumption that $d\psi_{K^+}$ and $d\psi_{Cl^-}$ are of the same order, or greater than, $d\psi_{H^+}$ and $d\psi_{OH^-}$ must also be made. This is satisfactory when one considers that the KCl activity is being varied over a wide range and that $d\psi_{H^+}$ and $d\psi_{OH^-}$ are expected to alter only very slightly, if at all, when KCl is dissolved in water.

Hence $\int K^+ d\psi_{K^+}$ and $\int Cl^- d\psi_{Cl^-}$ are very much greater than either $\int H^+ d\psi_{H^+}$ or $\int OH^- d\psi_{OH^-}$ and equation 2 reduces to

$$d\gamma = - \int H_2O d\mu_{H_2O} - \int K^+ d\psi_{K^+} - \int Cl^- d\psi_{Cl^-} \ldots \ldots \ldots \ldots (7)$$

Equation (7) can be obtained by simply ignoring the dissociation of the solvent at the outset (69), however this obscures the possible importance of pH changes.

Invoking the Gibbs convention (i.e. that $\int H_2O = 0$, refer Appendix 1), equation (7) reduces to

$$d\gamma = - \int KCl (d\psi_{K^+} + d\psi_{Cl^-}) \ldots \ldots \ldots \ldots (8)$$

Introducing activity coefficients on the molarity scale, the chemical potentials of $K^+$ and $Cl^-$ may be expressed as

$$\mu_{K^+} = \mu^0_{K^+} + RT \ln (Y + C_{K^+})$$

and

$$\mu_{Cl^-} = \mu^0_{Cl^-} + RT \ln (Y - C_{Cl^-})$$

Noting that $C_{K^+} = C_{Cl^-} = C_{KC1}$ and that $Y^+ = (Y + Y^-)^1/2$ by definition,

$$d\gamma = -2RT \int KCl d \ln (Y^+ C_{KC1})$$

i.e. $\frac{1}{4.606RT} \cdot \frac{d\gamma}{d \log_{10} (Y^+ C_{KC1})} = \int KCl \ldots \ldots \ldots \ldots (10)$
In Figure 4.7 surface tension has been plotted as a function of \( \log_{10}(Y + C_{KCl}) \); thus \( \Gamma_{KCl}^{(1)} \) has been evaluated.

At a bulk concentration of 3 molar \( \Gamma_{KCl}^{(1)} \) is \(-0.67 \times 10^{-10}\) moles cm\(^{-2}\). Assuming a purely arbitrary interfacial thickness of 10 Å, this corresponds to a concentration of \(-0.67\) molar. Hence KCl has been drastically excluded from the interface!

As has been already noted above, on comparing the values for various salts at the same bulk concentration and, provided the salts are of the same type (e.g. uni-univalent), one would expect that the higher the \( \Delta \gamma \) value, the larger will be the surface deficit.

Thus for the alkali metal chlorides, ammonium chloride and tetramethyl ammonium chloride one would expect the following sequence to be established, on the basis of the results quoted in Table 4.3.

\[
\Gamma_{LiCl}^{(1)} > \Gamma_{NaCl}^{(1)} > \Gamma_{KCl}^{(1)} > \Gamma_{RbCl}^{(1)} > \Gamma_{NH_{4}Cl}^{(1)} > \Gamma_{CsCl}^{(1)} > \Gamma_{TMACl}^{(1)}
\]

The magnitude of \( \Gamma_{i} \) should decrease from left to right and a similar conclusion should arise for MgCl\(_2\) and CaCl\(_2\).

Surface tension data for all salts at all concentrations have not been measured here, however they are available for NaCl, KCl and NH\(_4\)Cl (51, 52). Insufficient data were available for other salts to permit reliable estimates of the surface excesses to be made. A similar graphical plot and calculation as above yielded the required surface excesses, tabulated in Table 5.3 below along with the relevant \( \Delta \gamma \) data (refer to Appendix IV for details).
The calculations show that $\Gamma^{(1)}_{\text{NaCl}} > \Gamma^{(1)}_{\text{KCl}} > \Gamma^{(1)}_{\text{NH}_4\text{Cl}}$ at the same bulk molal concentration, paralleling the order of the $\Delta \gamma$ values. The sequence is consistent with the idea of a more disorder promoting species such as $K^+$ being preferred in the interface over that of $Na^+$, with its less favourable "structural entropy". It seems highly probable that similar conclusions can be drawn for the other salts (e.g. LiCl and CsCl), wherever there are differences in their surface tension elevations. The importance of structural effects and preferential exclusion of electrolyte becomes increasingly evident in following sections.
5.2 Equilibrium Spreading Pressures of n-octadecanol

The equilibrium spreading pressure (ESP) of an insoluble amphipathic compound is a quantity which is inherently difficult to measure, since a true equilibrium may not be reached due to evaporation and solubility of the substance at the temperature considered. It has been shown that (21, 23) loss of the monolayer is due almost entirely to evaporation, becoming more pronounced at high surface pressures. That this is to be excepted on theoretical grounds has been shown by Mansfield (22), in an argument based on the Gibbs Equation.

A constant surface pressure does not necessarily indicate the attainment of an actual ESP, since the net rate of spreading of the molecules from the bulk phase may be equal to the net rate of loss from the film. This condition is known as the steady state spreading pressure (SSSP, will be lower than the ESP) and is related to the ratio of crystal perimeter to film area. In fact for the case of hexadecanol, Roylance and Jones (21) have discovered that a perimeter/area ratio of $2 \times 10^{-2}$ cm$^{-1}$ was necessary for the SSSP to exceed 30 dyne cm$^{-1}$. The accepted ESP of hexadecanol is about 40 dyne cm$^{-1}$ at 25°C. Fortunately n-octadecanol is more involatile and insoluble at 21°C than hexadecanol (24, 25, 58), further reducing the likelihood of film loss. In this investigation the attainment of a true thermodynamic ESP has been assured by using a large excess of n-octadecanol crystals on a relatively small area and by isolating the experimental system from external influences.

Due to its state of extreme purity, impurities in the alcohol are considered to be absent. Moreover the experimental curves, after reaching the ESP value, showed no tendency to drift to lower pressures with time, a factor which Brooks and Alexander (26) ascribed to impurities
in their samples. This latter behaviour is consistent with the idea that impurities would change the composition of the spreading surface.

The question of possible alcohol hydrate formation is a more subtle problem in that it may influence the attainment of a true ESP. Trapeznikov (27) postulates that hydrates are formed in both film and bulk phases. Discontinuities in ESP/temperature curves, appearing at lower temperatures than similar breaks exhibited in simple cooling curves, provide the evidence for his assertion. This work has been extended by Stewart (28) and by Brooks and Alexander (26). In particular the latter have shown that the breaks observed in the thermal curves corresponded to a phase transition for tetradecanol and hexadecanol crystals. It should be stressed here that the existence of alcohol hydrates has only been inferred and that there is no direct evidence relating to their formation. In point of fact they are extremely rare and no hydrate of any straight chain alcohol crystal has been reported (29). With the above in mind, the influence of water and various concentrations of KCl on n-octadecanol was carefully examined. There was no detectable difference in the ESP's at 21°C of virgin crystals compared with those which have been exposed to water and/or KCl. Although this does not eliminate the possibility of alcohol hydrate formation, it at least illustrates that the ESP value is unaffected.

It is also highly likely that grinding the crystals may induce distortions in the crystal lattice, which would be expected to lead to increased spreading. Preliminary experiments showed that grinding produced ESP's 2 to 3 dyne cm\(^{-1}\) higher than those recorded with the normal crystals, hence the latter were chosen as the stable bulk phase. Comparison with other workers (30, 26, 24, 57) showed that there was considerable variation in the ESP results quoted for long chain alcohols
in general. In most cases the samples used were in powdered form and the ESP's were slightly higher than those measured here.

**TABLE 5.4** ESP for n-C\textsubscript{18}OH on water

<table>
<thead>
<tr>
<th>(\pi_e), dyne cm(^{-1})</th>
<th>°C</th>
<th>Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>(this work) 32.1</td>
<td>21</td>
<td>crystals</td>
</tr>
<tr>
<td>(ref. 26) 35 - 37</td>
<td>21</td>
<td>powder</td>
</tr>
<tr>
<td>(ref. 24) 35</td>
<td>25</td>
<td>---</td>
</tr>
</tbody>
</table>

* no known ESP work has been performed with long chain alcohols on concentrated salt solutions.

It has been found that the ESP of n-octadecanol, on an aqueous substrate containing KCl, increases with salt concentration. This increase, at a specified KCl concentration, matches the elevation of the surface tension of water by the salt, within experimental error, as can be seen by referring to Table 4.4 and Figure 4.6. There is a greater tendency for molecules to leave the bulk crystal when the substrate contains KCl, due to the increased surface free energy of the bulk KCl solution over that of pure water.

Recalling that \(\pi_e\) is defined as \(\pi_e = \gamma_o - \gamma_e\), \(\gamma_e\), the surface tension of an aqueous surface covered by an insoluble monolayer in equilibrium with the crystal, can be evaluated (see Table 4.4). Within the accuracy of the measurements the \(\gamma_e\) value is the same in all cases, no matter what the KCl concentration is, the average value of all determinations being (40.1\(^+\).6) dyne cm\(^{-1}\).

More explicitly, following 5.1 one can write

\[
d\gamma = - \int H_2O d\psi_{H_2O} - \int K^+ d\psi_{K^+} - \int Cl^- d\psi_{Cl^-} - \int ROH d\psi_{ROH}
\]

where the various terms are self-explanatory (refer Appendix I; ROH represents octadecanol). Choosing \(\int H_2O = 0\) and noting that because
the monolayer is in thermodynamic equilibrium with the crystal, 
\[ d\psi_{\text{ROH}} = 0, \quad \text{the above equation reduces to} \]
\[ \frac{d\psi}{d\ln Y^\pm_{\text{KCl}}} = -2RT \int_{\text{KCl}}^{(1)} \ln (Y^\pm_{\text{KCl}}) \]
and 
\[ \frac{d\psi}{d\ln Y^\pm_{\text{KCl}}} = 0 = -2RT \int_{\text{KCl}}^{(1)} \]
thus \[ \int_{\text{KCl}}^{(1)} = 0. \]
Hence there is no surface excess of salt in the presence of a monolayer in equilibrium with a crystal. Relative to the monolayer free aqueous surface, there has been a transferral of salt from the bulk into the interface i.e. positive adsorption of salt has occurred, and the interface and bulk both contain equal concentrations of salt and solvent. The importance of this point is illustrated later.

(* The reasonable assumption has also been made here that the octadecanol crystals are unchanged in their properties by contact with salt solutions of different concentrations).
5.3 The Surface-Pressure - Area/molecule Isotherms for n-octadecanol on Aqueous Substrates.

To recapitulate, the $\Pi$ - A isotherms indicate the following features (see Figs. 4.1 to 4.5 and Appendix VI).

1. All the salts examined cause a marked expansion of the low pressure-high area "liquid" region of the $\Pi$-A isotherms. The extent of this expansion is directly proportional to their elevation of the surface tension of water and decreases according to the following sequence:

$$
\text{Mg}^{2+} \succ \text{Ca}^{2+} \succ \text{Li}^+ \succ \text{Na}^+ \succ \text{K}^+ \succ \text{Rb}^+ \succ \text{NH}_4^+ \succ \text{Cs}^+ \approx \text{TMA}^+ ,
$$

at 4 molar with Cl$^-$ as the reference anion. There is reasonable correlation with data indicating the structure making/breaking nature of individual ions (see chapter 2), although there are some obvious discrepancies. This highlights the care which must be exercised when assessing any one set of evidence relating to water structure effects. In general structure breakers such as Cs$^+$, Rb$^+$ do not expand the $\Pi$-A curves as much as structure makers like Li$^+$, Mg$^{2+}$, a reflection of their smaller elevation of the surface tension. The thermodynamic significance of the $\Pi$-A curves is discussed in the next section.

2. A decrease in salt concentration as shown for KCl in Figure 4.3 is accompanied by a decrease in expansion in the "liquid" region of the $\Pi$-A curve. Since the limiting areas are unaffected in all cases, this indicates the absence of inclusion complexes between the cations and the -OH head groups of the monolayer.

3. Within experimental error, a comparison of the results at 4 molar for (RbCl, NH$_4$Cl) and (CsCl, TMACl), each pair having comparable surface tensions, shows that the $\Pi$-A curves superimpose, indicating the absence of specific salt effects.
It is important at this point to consider whether the results found are due to artifacts. It is extremely unlikely that surface active impurities are the cause of the expansion of the $\Pi$-A isotherms, in view of the precautions taken in the experimental work and of the nature of the high purity reagents used. There is the likelihood that Al$^{III}$ species may be present due to the release of trough material up through small perforations or pinholes in the Teflon coating. However the addition of small amounts of aluminium chloride produced no discernible change in the pressure-area curves of n-octadecanol on water. Combined with the agreement of the Ao value with that quoted by Gaines (24), this leads one to assert that such dissolution is negligible and has no effect.

Film loss due to evaporation and solubility has already been covered in a previous section. Moreover Brooks and Alexander (26) found that high concentrations of ammonium sulphate in the subphase had no appreciable effect on the rate of film loss, hence it would appear that errors due to evaporation and/or solubility of the alcohol are negligible. It may be argued that because evaporation at high pressures is more pronounced and that the same experimental conditions as in the ESP measurements do not apply here (i.e. a large excess of crystals), evaporation may be important (e.g. film loss at 40$^\circ$C and 35 dyne cm$^{-1}$ is 0.12% of the film per minute (23, 24)). However as the amount of material spread during each run is quite considerable (about 0.1 mg) and the time for which the monolayer, at 21$^\circ$C, is above a pressure of 10 dyne cm$^{-1}$ is short (less than 1 minute), film loss can be overlooked.

A less obvious source of error may be involved due to adsorption of ions on to the surface of the mica plate. This is a process which could feasibly alter the free energy relationships existing at the interface.
resulting in a finite contact angle $\Theta$ and consequently invalidating an assumption made in the Wilhelmy plate technique (i.e. that for a completely wetted surface, $\Theta$ is assumed zero). Indeed this adsorption process has been shown to be the case for a potassium chloride subphase in the ESP measurements, where epitaxing of KCl on the mica occurred, consequently producing much lower ESP values than in the case of a platinum plate, since with the latter, surface adsorption of ions does not occur, its absence being demonstrated in blank runs. This is in direct contrast to the increase in $\Pi$ observed in the $\Pi$-A runs, where a mica plate was used. A considerable amount of time elapses (several hours) before there is a significant build up of crystals on the mica plate and blank runs performed on the Langmuir Trough, that is in the absence of monolayer, showed that zero pressure was registered throughout the duration of a normal run. Furthermore, within experimental error, there is no difference between the surface tension of salts measured with a platinum than with a mica plate. Although it is important to use a platinum plate for the ESP data, because the plate is dipping into the substrate for many hours, it appears that the elevation of surface pressure is not due to an artifact involving the mica plate (i.e. adsorption has no effect on contact angle; over a long period of time its only effect is to reduce the measured $\Pi$ by increasing the weight of the mica plate.)

Although there have been numerous studies on the effect of salts on charged monolayers at the air/water interface (see 5.5), there has been very little work published on uncharged polar molecules, especially on concentrated salt solutions. The following paragraphs are devoted to a consideration of neutral monolayers.
The $\Pi$-A isotherms of n-octadecanol on water at various temperatures are well characterized (24) and it has been shown that changes of pH over the range 2 - 10 have no effect on the properties of long chain alcohol monolayers. Neither do dilute salt solutions exert any appreciable effect on their $\Pi$-A characteristics. A consideration of Zisman's data (59) shows a slight but distinct expansion of the $\Pi$-A isotherm of octadecanol on dilute ($5 \times 10^{-4}$ M) Th(NO$_3$)$_4$ at $11^\circ$C, a feature which Zisman has neglected. This result is to be expected in view of the expected elevation of surface tension caused by that salt.

Lange (60) has examined the effect of electrolyte in the substrate on the pressure-area curves of polyoxyethylene n-dodecanol. Data from his work illustrate that for a specified monolayer at constant area per molecule, there is a continuous increase in $\Pi$ with increasing NaCl concentration. Making the point that whereas $\Pi$ at constant area decreases with increasing electrolyte concentration for charged monolayers, due to a reduced Coulombic repulsion between head groups, it emphasises that the effect of electrolyte should have virtually no effect on nonionic surfactants, since electrical interaction is negligible. Thus the observation of the completely reverse effect is "... unexpected and difficult to explain" (60). A reduction in hydration of the polyoxyethylene chains in concentrated NaCl is suggested as a possible explanation, since this would be accompanied by a decrease in immersion of the chains, followed by an increase in area per molecule and therefore in $\Pi$. This is not a full explanation since examination of the $\Pi$-A isotherms for n-dodecanol with 2 and 6 ethylene oxide groups indicates that at $60 \text{ Å}^2$ per molecule and above, the increase in $\Pi$ is comparable to the elevation of surface tension by the 5M NaCl (i.e. about 7 dyne cm$^{-1}$). At a fixed area, however, $\Pi$ increases with addition of ethylene oxide groups.
The observed expansion is probably due to two factors, the first of which has been overlooked by Lange, viz

(a) the elevation in \( \gamma \) caused by the salt.
(b) the increase in \( \Pi \) caused by a decrease in hydration of the ethylene oxide groups.

Recently (61) the effect of urea on unionized stearic acid monolayers has been studied. Urea expands the "liquid" region of the \( \Pi - A \) isotherms and this is explained in terms of a dipole-dipole interaction between the urea molecules and the terminal carboxyl groups. An increase in urea causes an increase in \( \Pi \), due to the increased probability of a urea molecule being associated with a carboxyl group. Since urea does not elevate the surface tension of water to any appreciable extent (e.g. \( 0.56 \) dyne cm\(^{-1}\) at 37°C for 5 molar urea), on the basis of the work carried out in this investigation negligible expansion should be observed, unless specific interaction is present. The pressure-area (62) isotherms of unionized stearic acid have been studied on D\(_2\)O and compared with those on H\(_2\)O. Although there is no apparent alteration of the \( \Pi - A \) characteristics, surface potential/area and viscosity/surface pressure data indicate the general importance of water structure at the interface.

The above comparisons highlight the lack of data available on the behaviour of uncharged films on concentrated salt solutions and the absence of knowledge about the role of interfacial water beneath these monolayers.
5.4 Thermodynamic Analysis of Pressure/Area Data.

In examining data obtained from the $\Pi$-A isotherms, the system of monolayer/KCl/water is considered to be at equilibrium since the application of the Gibbs Equation is valid only under this condition. Whether or not a $\Pi$-A isotherm represents an equilibrium situation is debatable, since the alcohol monolayer is compressed at a slow, but constant rate. Although the rate of compression used here is almost identical to that used by other workers (61, 62) for similar monolayers (i.e. about $3A^2$ per molecule per minute), it was thought wise to test the assumption of equilibrium. The absence of any significant alteration in pressure below 20 dyne cm$^{-1}$, monitored continuously for a period of three to five minutes when compression of the alcohol monolayer was stopped, indicated the validity of assuming equilibrium for moderate surface pressures. At high pressures this test is not applicable, since leakage is pronounced. Since the areas chosen from the $\Pi$-A curves (i.e. 21, 20A$^2$) fall within this medium pressure range, the data is amenable to analysis with the Gibbs Equation.

The results illustrated for potassium chloride in Figures 4.7 and 4.8 and tabulated in Appendix V show that $d \gamma/d \ln Y^+ \propto C_{KCl}$ at a specified area per molecule, decreases as that particular area per molecule is reduced. The slope has a value of zero at the point where the equilibrium surface tension has been reached (see 5.2). These features can be interpreted quantitatively using the Gibbs Equation (refer to Appendices I and II for details).

At constant temperature and pressure the variation of interfacial tension can be written, as before,

$$ + d \gamma = -\sum \int d\psi $$

.................(1)
In the system considered here, the principal species are $\text{H}_2\text{O}$, $\text{K}^+$, $\text{Cl}^-$, $\text{H}^+$, $\text{OH}^-$ and $\text{ROH}$, where $\text{ROH}$ represents n-octadecanol. Hence,

$$
+\frac{d\gamma}{RT} = -\int \text{H}_2\text{O} \, d\gamma_{\text{H}_2\text{O}} - \int \text{H}^+ \, d\gamma_{\text{H}^+} - \int \text{OH}^- \, d\gamma_{\text{OH}^-} - \int \text{K}^+ \, d\gamma_{\text{K}^+} - \int \text{Cl}^- \, d\gamma_{\text{Cl}^-} - \int \text{ROH} \, d\gamma_{\text{ROH}} \ldots \ldots \ldots \ldots (2)
$$

Recalling section 5.1, one can show that

$$
+\frac{d\gamma}{RT} = -\int \text{H}_2\text{O} \, d\ln a_{\text{H}_2\text{O}} - \int \text{ROH} \, d\ln a_{\text{ROH}} - 2 \int \text{KCl} \, d\ln (Y^+ \text{C}_{\text{KCl}}) \ldots \ldots \ldots (3)
$$

Although surface excesses can be calculated on the basis of a number of conventions (see Appendix 1), it would not serve any real purpose to alter the convention chosen here i.e. that $\int_{\text{H}_2\text{O}} = 0$, since all one is interested in is noting alterations in a surface excess - one convention serves equally as well as the other for this purpose.

Invoking the Gibbs convention, (3) is reduced to

$$
+\frac{d\gamma}{RT} = -\int \text{ROH} \, d\ln a_{\text{ROH}} - 2 \int \text{KCl} \, d\ln (Y^+ \text{C}_{\text{KCl}}) \ldots \ldots \ldots (4)
$$

where the various $\int$'s now are adsorption densities relative to zero surface excess of solvent.

Further manipulation yields

$$
+\frac{1}{RT} \frac{d\gamma}{d\ln (Y^+ \text{C}_{\text{KCl}})} = -\frac{\int \text{ROH} \, d\ln a_{\text{ROH}}}{d\ln (Y^+ \text{C}_{\text{KCl}})} - 2 \int \text{KCl} \ldots \ldots \ldots (5)
$$

At the point where equation (2) is reached, an assumption may be made (e.g. ref. 61) that since the surface concentration of alcohol is held constant, $d\gamma_{\text{ROH}} = 0$. Although this is true for the ESP measurements, which was the reason for performing them, it is not necessarily the case here. Examination of equation (5) reveals that this assumes that the activity of the alcohol does not change with salt activity. It is possible that the activity of the dissolved long chain alcohol, though dilute, may change with an increase in salt concentration. Long and McDevitt
(63) have made a study of the activity coefficients on non-electrolyte solutes in aqueous salt solutions. Although there is no specific data on long chain alcohols, in general there is considerable variation in activity coefficient as a function of salt concentration. Akerlof (64) has discovered a marked change in the activity coefficient of diacetone alcohol, in dilute aqueous solution, with KCl concentration. He finds that in 4 molar KCl solutions, the alcohol activity coefficient is approximately 2, thus \[ \frac{\delta a_{ROH}}{\delta a_{KCl}} \] is positive.

Shaw and Butler (65) have studied the behaviour of ethyl alcohol in concentrated aqueous solutions of LiCl. For large amounts of ethyl alcohol they find a decrease in alcohol activity with increasing LiCl concentration (i.e. \( \frac{\delta a_{ROH}}{\delta a_{LiCl}} \) is negative,) whilst exactly the reverse behaviour is found for small quantities of ethyl alcohol in solution. Apart from these two studies, 'no systematic examination of the activity coefficient variation of long chain alcohols in electrolyte solutions has been made.

The crux of the problem lies in choosing a value for \( \frac{\delta \ln a_{ROH}}{\delta \ln (Y^+ C_{KCl})} \). This quantity is virtually impossible to determine experimentally, other than by extrapolation from activity data for shorter chain alcohols. Even a similar analysis to that carried out by Weil (44) results in exactly the same problem.

However referring to Figure 4.3 it can be seen that, for any bulk KCl concentration, the surface pressure at an area per molecule of 25Å² is zero. Hence from the definition of surface pressure, it is obvious that \( \gamma = \gamma_0 \) o i.e. at 25Å² per molecule, the presence of the monolayer has no effect on the surface tension of the KCl solutions. Recalling section 5.1, it has already been shown that the surface excess of KCl may be calculated from
\[ \frac{1}{RT} \frac{d \gamma}{d \ln (Y^+ C_{KCl})} = -2 \int_{KCl}^{(1)} \] (see section 5.1, equation 10)

Since the monolayer does not affect the surface tension of the salt solution at an area per molecule of \(250^2\), these terms will have precisely the same form and value in equation (5) above.

Thus at \(250^2\), \(\frac{d \ln a_{ROH}}{d \ln (Y^+ C_{KCl})}\) must equal zero.

In view of the fact that the alcohol is highly insoluble it is unlikely that further compression of the monolayer to \(21\) or \(200^2\) per molecule will alter the value of \(\frac{d \ln a_{ROH}}{d \ln (Y^+ C_{KCl})}\).

Hence in the absence of further evidence, one must consider that the ideal situation applies (i.e. no variation of alcohol activity with salt concentration), and thus \(d \ln a_{ROH} = 0\).

Under these conditions,

\[ - \frac{d \gamma}{d \log_{10} (Y^+ C_{KCl})} \times \frac{1}{4.606 \ RT} = \int_{KCl}^{(1)} \] (6)

It should be stressed here that the above problem does not arise when calculating surface excesses in the absence of a monolayer, nor in the case of ESP measurements.

Equation (6) has been used to calculate surface excess data from Figures 4.7 and 4.8 (refer Appendix V for details). These quantities are tabulated below in Table 5.5 for a bulk concentration of 3 molar, similar results being obtained for other bulk concentrations.

In order to assign bulk concentration values to the various surface excess quantities, a purely arbitrary interfacial thickness \(\gamma^0\) of 10A has been chosen. Although this is hardly a macroscopic phase, in view of the difficulties concerned with assigning interfacial dimensions (refer Chapter 2) there is no real alternative.
TABLE 5.5 Surface excesses of KCl in the presence and absence of an n-octadecanol monolayer at 21°C.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>$\frac{d}{d\log_{10}(Y^+ C_{KCl})}$</th>
<th>$\Gamma^{(1)}_{KCl} \times 10^{-10}$ moles cm$^{-2}$</th>
<th>$\Gamma^{(1)}_{KCl}$, moles l$^{-1}$ assuming $\gamma = 10^A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(see 5.1) no monolayer</td>
<td>7.5</td>
<td>-0.67</td>
<td>-0.67</td>
</tr>
<tr>
<td>21Å$^2$ per molecule</td>
<td>5.0</td>
<td>-0.45</td>
<td>-0.45</td>
</tr>
<tr>
<td>20Å$^2$ per molecule</td>
<td>4.0</td>
<td>-0.36</td>
<td>-0.36</td>
</tr>
<tr>
<td>(see 5.2) area at ESP</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

It is apparent that as compression of the monolayer occurs, the surface excess becomes increasingly positive. Salt is transferred into the interface and, relative to the monolayer free surface, positive adsorption has occurred. This process continues until the surface and bulk concentrations are equal, at which point the surface tension corresponding to that at the ESP is reached.

In examining the surface excess of urea under stearic acid monolayers, Sears (61) has used an expression

$$\left(\frac{1}{RT} \times \frac{\Delta \Pi}{\Delta x}\right)_A = \left(\frac{1}{1 - x}\right)^2 \frac{\Pi_2 - x \Pi_1}{(1 - x)}$$

where $x$ is the mole fraction of urea, $\Pi_2$ its surface concentration and $\Pi_1$ refers to the surface concentration of water. The urea concentrations vary from one to five molar and, since $x < 1$,

$$\left(\frac{1}{RT} \times \frac{\Delta \Pi}{\Delta x}\right)_A \sim \frac{\Pi_2}{x}$$

An analogous expression can be arrived at for KCl (see Appendix III) provided one assumes $\bar{u}_{ROH} = 0$ and that the mole fraction activity coefficient of KCl is unity. This latter assumption is very unlikely for either KCl or urea in concentrated solutions.
The paper by Sears infers that \( \int \text{urea} \) represents a total surface concentration. This is erroneous as shown in Appendix III. In fact the \( \int \text{KCl} \) values (or \( \int \text{urea} \)) arrived at in this way are equivalent to choosing the convention \( \int \text{H}_2\text{O} = 0 \). They are relative adsorptions and are shown below in Table 5.6 as a means of comparing them with those obtained in the previous analysis. The \( \frac{d\gamma}{dx} \) values have been obtained from Figures 4.9, 4.10 and 4.11 and reference should be made to Appendix V for the relevant data concerning these diagrams.

**TABLE 5.6**  
Surface excesses of KCl in the presence and absence of an n-octadecanol monolayer. (calculations of \( \Gamma^{(1)} \text{KCl} \) at 3 molar bulk concentration where the mole fraction of KCl = 0.0512)

<table>
<thead>
<tr>
<th>Conditions</th>
<th>( \frac{d\gamma}{dx} )</th>
<th>( \Gamma^{(1)} \text{KCl} \times 10^{-10} ) moles cm(^{-2} )</th>
<th>( \Gamma^{(1)} \text{KCl}, \text{ moles} \text{ cm}^{-2} \text{ assuming } \gamma = 10 \text{ A} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>no monolayer</td>
<td>86.7</td>
<td>-0.91</td>
<td>-0.91</td>
</tr>
<tr>
<td>21Å per molecule</td>
<td>49.0</td>
<td>-0.51</td>
<td>-0.51</td>
</tr>
<tr>
<td>20Å per molecule</td>
<td>44.6</td>
<td>-0.47</td>
<td>-0.47</td>
</tr>
<tr>
<td>area at ESP</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Exactly the same conclusions can be drawn here as for the previous analysis i.e. there is transferral of KCl into the interface as the monolayer is compressed. The differences between the \( \Gamma^{(1)} \text{KCl} \)'s in the 2 methods can be attributed to neglecting activity coefficients in the second case.
5.5 Surface tension is a function of intermolecular attraction and orientation within an ordered interfacial region (31) hence, with reference to previous sections, certain conclusions can be arrived at regarding the behaviour of this structured region. Exclusion of electrolyte from the ordered interface occurs, the surface excesses involved being calculable in the case of sodium chloride, potassium chloride and ammonium chloride, as is illustrated in section 5.1. Furthermore using as examples the alkali metal chlorides, though a similar reasoning can be applied to the pairs (NH$_4^+$, TMA$^+$) and (Mg$^{2+}$, Ca$^{2+}$) the amount of exclusion increases as the structural entropy contribution of the metal cation becomes more negative. This indicates the preference for ions in the interface which are able to disorder the structure existing there. Drawing on the surface pressure-area per molecule results established for the case of potassium chloride, it is apparent that, at the same bulk concentrations, relatively more molecules of lithium chloride have been transferred into the interface at any given area per molecule compared with caesium chloride. Reference to the Π-A isotherms for the 4 molar salts at a specified area reveals an isothermal (and virtually isobaric, since $dP \approx 0$) increase in surface pressure from caesium to lithium. Mechanical work is involved in order to reach this specified area and can be expressed as

$$\Delta G \text{ compression} = \int^{A_2}_{A_1} \gamma \, dA$$

For the same limits, $\Delta G \text{ comp} \overset{\text{LiCl}}{\geq} \Delta G \text{ comp}$. Thus it requires more work to compress a monolayer on a lithium chloride subphase and so transfer the more numerous, strongly hydrated Li$^+$ with their less favourable entropy than the poorly hydrated caesium ions, where a smaller number of disorder promoting species is involved.

To examine the entropy considerations more closely requires a knowledge of the Π-A isotherms at various temperatures for each salt.
Noting that \( \mathcal{S} = -\frac{(d\tilde{\chi})}{(dT)A} = \frac{(d\Pi)}{(dT)A} \) where \( \mathcal{S} \) is the surface entropy per unit area and thus

\[
S = \frac{A}{dT} \frac{d\Pi}{A}
\]

such a study would then allow a comparison of surface entropy changes as the metal cation is varied. Recalling that the monolayer structures the underlying substrate, a variation in \( A \frac{d\Pi}{dT} \) with the metal cation will then refer directly to the interface structure. Although the treatment has not been performed in this investigation, the results of Sears and Schulman (46) may be used for comparison. These workers have plotted \( A \frac{d\Pi}{dT} \) versus \( A \) for stearic acid monolayers on substrate solutions containing 0.5M LiOH, KOH and NaOH. At the same area per molecule, \( A \frac{d\Pi}{dT} \) decreases in the sequence \( K^+ \gg Na^+ \gg Li^+ \), which is consistent with the idea of greater disorder existing in the interface (all other parameters constant) in the case of \( K^+ \) than with \( Li^+ \), as has been proposed here.

As indicated in Figures 4.7 to 4.11 and in Tables 5.5 and 5.6, salt is gradually transferred into the surface region until the \( \gamma \) e value of the surface tension, which is independent of salt concentration, is reached. It would therefore seem that the most favourable interface structure, in the presence of an alcohol monolayer at a surface pressure equal to its ESP, involves equal surface and bulk concentrations of salt, since in this case maximum randomness in the system of salt/monolayer/water has been achieved. Any change from this situation (i.e. salt transfer in or out of interface) involves a decrease in the entropy of the system. At equivalent bulk concentrations, structure breakers such as \( Cs^+ \) are transferred more easily into this structured region than structure breakers such as \( Li^+ \), for reasons which have been already discussed above, although
both are preferentially excluded from the air-water interface.

It is difficult to see how compression of an essentially neutral monolayer could result in the transfer of ions into an interface, if the forces responsible for their surface deficit were due solely to electrostatic interactions tending to pull them into the bulk. It would appear that the overriding factor responsible for salt transferral is an entropy effect, connected jointly with structuring of the interface by the monolayer and with water-salt interactions.

The ion effects reported above have counterparts in other systems. Siever (32) has discovered that interstitial water extracted from cores of mud taken from the sea floor is more saline than the overlying "bottom" water, and attempts to explain this in terms of the clay-water system acting as a semi-permeable membrane, restraining the hydrated ions. In a similar vein, Horne (34, 134) remarks on the fact that ionic fractionation also occurs at the sea-water/air interface, the salt ratios in sea spray generally being smaller than those in the ocean water. In a study of the exclusion of cations from silica gels, McConnell (33) found good correlation between the experimental values obtained and the structure making/breaking properties of the ions as indicated by their viscosity B coefficients. Horne (34) has examined the structure of interfacial water at the solid/liquid interface, by determining the effect of hydrostatic pressure on the electrical conductivity of alumina particles permeated with aqueous potassium chloride solutions. At the pressures worked at (i.e. greater than 2000 Kgm/cm²) the structure of bulk water is completely destroyed, hence the results are interpreted in terms of an interfacial water structure (β form) which is stable to pressure and less susceptible to thermal destruction than normal bulk water (α form). Horne's results indicate that this enhanced water
structure near the solid alumina surface excludes electrolyte, the resulting increase in electrolyte in the unbound water being detected by elution and conductivity measurements. When electrolyte solutions contact activated carbon, there is simultaneous adsorption of solute on the solid surface and exclusion from the liquid near the solid/liquid interface (50). There is a tendency for the least hydrated ions to be excluded from the surface region less than more strongly hydrated species, suggesting that solvent layers on the carbon surface may be responsible.

Schick and Gilbert (35) have studied the effect of urea and guanidinium chloride on the critical micelle concentration (C. M. C.) of a non-ionic detergent (a polyoxyethylene straight chain alkanol). Hydration of the ethylene oxide side chain is increased, due to the structure breaking effects of urea and GuCl, with a consequent increase in CMC due to the hindering of micelle formation. In a further study (36) on the effect of electrolyte on  n-dodecyl sulphates, the decrease in the CMC in the order \( \text{Li}^+ > \text{Na}^+ > \text{TMA}^+ \) is attributed to diminished hydration of the cations. There is correlation between structure making and breaking effects, a structure promoting ion such as \( \text{TMA}^+ \) enhancing micelle formation whereas a structure breaking one (e.g. \( \text{Na}^+ \)) reducing it. This very marked behaviour of \( \text{TMA}^+ \) is not evident in the results reported in this investigation.

Goddard et al. (37) have compared the \( \Pi-A \) isotherms of various long chain fatty acids at high pH on electrolyte solutions containing \( \text{Li}^+, \text{Na}^+, \text{K}^+, \text{TMA}^+ \) and \( \text{TEA}^+ \) in low concentration. The cations condense the monolayers in the order \( \text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{TMA}^+ > \text{TEA}^+ \), a sequence which is directly in reverse to that found here.
In order to explain these effects, application of the Davies (40) equation of state to the pressure-area data is performed. Reasonable agreement is achieved for a particular cation and a specific set of conditions, however this is not so when either the cation type or ionic strength is changed. Similarly the Fowkes (38) and Lucassen-Reynders (39) equations of state overestimate the pressure when applied to these $\Pi$-$A$ curves, since they assume "ideal" surface behaviour. No allowance is made in either of these forms for non-ideality due to changes in ion type, ion-solvent interactions or concentration changes.

A similar study by the same workers (41) involves the alteration of the $\Pi$-$A$ isotherms of sodium docosyl sulphate monolayers (i.e. having $-N^+\left(CH_3\right)_3$, $-N^+H\left(CH_3\right)_2$, $-N^+H_3$ as head groups) by various alkali metal chlorides, at concentrations not greater than $10^{-3}$ M. Expansion of the curves is in the order $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ which is the direct opposite of the study above, and in agreement with that found for n-octadecanol monolayers at high salt concentrations. This sequence is the same as the Hofmeister series relating to the flocculation of negatively charged colloids, and has previously been reported by Goddard (42) for the CMC lowering of ionic detergents. It is also the case for the interactions of cations with strong acid ion exchange resins (43). Again there is poor agreement between theoretical equations of state and the experimental results. The authors cannot account for the differences in behaviour of the ions other than qualitatively emphasising the importance of water structure and the need for including activity coefficients in theoretical equations of state. Also involved will be a knowledge of ion hydration and electrostatic interactions between ions, solvent and head groups. The embryonic overtones to this are made by referring to a specific interaction energy and a non-specific
electrical energy, however beyond stating that they exist, little progress is made.

Non-ideality in the surface behaviour of alkali metal cations has been portrayed by Weil (44) in a direct application of the Gibbs Adsorption Equation. A consideration of the surface behaviour of alkali metal salts of dodecyl sulphate reveals that, at equal surface excess concentrations, the surface tension decreases in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+$. Since the surface excesses are equal, the inter-chain cohesive forces are the same and any differences in surface tension are due to dissimilar ionic forces in the surface phase. There is satisfactory agreement between the data of Weil and that of Rogers and Schulman (45). The latter observed that, for octadecyl sulphates, the surface pressures of the alkali metal salts increase in the sequence $\text{K}^+ < \text{Na}^+ < \text{Li}^+$ at constant area. However exactly the reverse is found for the alkali metal salts of stearic acid (15). Therefore Weil suggests that the surface behaviour is analogous to that in concentrated solutions and expresses the Gibbs Equation in a form which relates the surface tension to activity in the surface phase. Predictions from the bulk activity behaviour of comparable anion-cation pairs then leads qualitatively to the observed sequence.

Parreira (47) has obtained the $\Pi$-A isotherms for dodecylpyridinium halides adsorbed at the air water interface. Expansion of the isotherms decreases in the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$ and is interpreted in terms of ion-pair formation between the film ions and the halide counterions. According to Parreira the positive potential exerted by the monolayer, coupled with a pronounced entropy effect, accounts for the accumulation of halide ions in the interface. Ion pairing is explained in terms of a water
structure enforced mechanism propounded by Diamond (48), which requires that the solvent be organized to some extent. This seems quite reasonable in view of the structure existing at the interface. The conclusion reached, that a noncoulombic energy term (accounting for specific interactions) should be included in theoretical treatments, is identical to that reached by other workers (37, 41, 44).

Villalonga et al (49) detected differences in the action of 0.15M subphase solutions of NaCl, KCl and LiCl on the \( \Pi \)-A behaviour of dipalmitoyl lecithin monolayers. Compared with water, the salts cause an expansion of the \( \Pi \)-A curves in the decreasing order \( \text{Na}^+ \approx \text{K}^+ > \text{Li}^+ > \text{H}_2\text{O} \). The net change on the lecithin monolayer is zero, due to the neutralization of the trimethylammonium and phosphate groups. Adsorption of cations on the phosphate groups accounts for the expansion, although there is no explanation in differences in action between \( \text{Na}^+ \), \( \text{K}^+ \) and \( \text{Li}^+ \). The authors indicate that this specific adsorption process may be related to the selective permeability of ions through cellular membranes. It should be noted that reagent grade chemicals were used without further purification for the preparation of the salt solutions. In view of some of the difficulties experienced in this present study (see chapter 3), a certain amount of caution should be exercised in evaluating the sequence of ion effects, at least in the case of the pressure-area isotherms.

Finally it seems pertinent to consider some consequences of the equation of state for charged monolayers originated by Davies (50), since this still influences contemporary thought. Although referring to a charged film, it highlights the deficiencies between experiment and theory. The Davies equation can be written as
\[
\Pi = \frac{kT}{A-A_0} + 6.1 \sqrt{C} \left\{ \frac{\cosh \sinh^{-1} \left( \frac{134}{A_0/C} \right)}{A_0/C} \right\} - \frac{400n}{A^{3/2}}
\]

refers to 2D gas behaviour, Ao as co-area term.

electrical contribution to the free energy of the monolayer Accounts for cohesion between hydrocarbon chains possessing n carbon atoms.

This is applied to films of \(C_{18}H_{37}N(CH_{3})_{3}^+\) on NaCl solutions at the air-water interface. At high salt concentrations (i.e. 0.1 to 2M) the observed pressure exceeds that calculated from the equation above (by 0.1 to 3.9 dyne cm\(^{-1}\), according to area per molecule and NaCl concentration). Thus it is obvious that the elevation of the surface tension of water by the salt (at 21°C, \(\Delta \gamma\) for 2M NaCl is ca 3.3), activity coefficients and specific ion effects must be included in this theoretical treatment.

The importance of ion-solvent interactions is, as delineated above, of paramount importance in explaining effects in a diversity of fields. The concept of exclusion of electrolyte at ordered interfaces is quite new, however it is essential in explaining the behaviour of mono-molecular films on electrolyte solutions. For a satisfactory theoretical description of their \(\Pi\)-A characteristics, the variety of solvent/solute/head group effects occurring in the structured interface must be accounted for.
SUMMARY.

In brief, the main conclusions of this investigation are as follows:

1. Inorganic salts are preferentially excluded from the air-water interface, the extent of this exclusion being directly related to the structure making/structure breaking tendencies of the ions concerned. Structure breakers are generally excluded to a smaller extent than structure makers.

2. Application of the Gibbs Adsorption Equation to experimental data has shown that, on compression of an n-octadecanol monolayer on an aqueous KCl solution or on forming a monolayer from the bulk crystal, salt is positively adsorbed at the interface, relative to the monolayer-free surface, until there is zero surface excess of salt. Less mechanical work is involved in transferring structure breakers into the interface compared with structure makers.

3. The salts examined cause a marked expansion of the low pressure-high area "liquid" region of the \( \Gamma - A \) isotherms. The extent of this expansion is directly proportional to their elevation of the surface tension of water and decreases according to the following sequence:

\[ \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ \sim \text{NH}_4^+ > \text{Cs}^+ \sim \text{TMA}^+ \]

at 4 molar with Cl\(^-\) as the reference anion.
FUTURE WORK.

Further work in this field may well proceed along the following lines:

1. The accurate measurement of surface tension data for all salts at all concentrations is required, in order that the surface excess quantities can be computed and compared with the conclusions drawn in this present investigation.

2. A study of the $\Pi$-A isotherms at various temperatures for each salt is advisable in order that further information may be obtained concerning the effects of ions on the structure of the interfacial region.

3. It may be useful to perform surface potential measurements, for similar reasons as cited in (2) above. In particular a record of the change in surface potential as a monolayer is formed from a bulk crystal on an aqueous salt solution should be very informative, since the surface potential will depend on the orientation of dipoles and the adsorption of ions at the surface of the aqueous electrolyte solution.

4. The study of evaporation resistance in monolayer/salt/water systems may also prove useful, since the existence of a structured interfacial region should prove a "barrier" to the escape of a water molecule into the atmosphere. Measurements may show an activation energy for this "barrier" and this in turn could relate to the interfacial structure (135).
APPENDIX I.

A. The adsorption of species at an interface can be calculated with the aid of the celebrated equation originally deduced by Gibbs (66). Although his treatment is mathematically precise, it is difficult to visualize and has been treated in a simpler fashion by Guggenheim (67, 68) and by Defay et al (69).

The variation of interfacial tension ($\gamma$) with temperature, pressure and chemical potential is given by:

\[ -d\gamma = S\,dT - \gamma\,dP + \sum_i \mu_i \,dN_i \ldots \ldots \ldots \ldots \ldots (1) \]

where $S$ is the entropy per unit area, i.e. $S = S/A$,

$N_i$ is the number of moles per sq. cm. in the surface layer,

$\mu_i$ is the chemical potential of species $i$,

$\gamma$ is the thickness of the interface,

$T$ is the absolute temperature and $P$ is the pressure.

At constant temperature and pressure this equation reduces to:

\[ -d\gamma = \sum_i \mu_i \,dN_i \ldots \ldots \ldots \ldots \ldots (2) \]

B. In the above equations, in order to assign specific numerical values to the surface excess of each component $i$, a certain mathematical surface must be chosen such that it is parallel to, and either within or in close proximity to, the region of discontinuity between the two bulk phases. Thus the surface excesses calculated in this way are then relative excesses.

The general equations deduced by Gibbs are valid for any choice of this surface, however the most favoured choice is the one which leads to zero surface excess of one of the components (normally the solvent). The resulting restricted equation is more commonly referred to as the Gibbs Adsorption Equation. However there are other conventions which may be used in place of that used by Gibbs.
and, in some instances, they are physically more realistic. Although admirably covered by Guggenheim, Defay and others (67 - 70), this material is briefly reviewed here in summary form.

Conventions relating to the \( \Gamma_i \)

The geometrical surface may be chosen according to a number of conventions:

1. The first involves the idea that a portion of the liquid containing unit area of surface contains \( \Gamma_i \) moles of each species more than a portion of the interior which contains exactly the same quantity of species (1) i.e. \( \Gamma_i^{(1)} = 0 \) (also known as Gibbs convention where (1) = solvent).

2. Convention (2) compares unit area of surface containing \( \Gamma_i \) moles of each species more than a portion in the interior which contains exactly the same number of moles of species (2) i.e. \( \Gamma_i^{(2)} = 0 \).

3. Thirdly, a portion of liquid with unit area of surface contains \( \Gamma_{i}^{(N)} \) moles of each species \( i \) more than a portion in the interior containing exactly the same total number of moles of all species i.e. \( \Gamma_{i}^{(N)} = 0 \).

4. According to the fourth convention one can define \( \Gamma_i \) as the number of moles of the species \( i \) in a portion of the liquid containing unit area of surface more than in a portion in the interior of exactly the same mass. i.e. \( \sum_{i} M_{i} \times \Gamma_{i}^{(M)} = 0 \) \( M_{i} = MW \) of species \( i \).

5. In conclusion \( \Gamma_i \) can be defined as the number of moles of the species \( i \) in a portion of the liquid containing unit area of surface more than in a portion in the interior of exactly the
same volume \( \bar{V} = \sum_i V_i \bar{v}_i = 0. \)

i.e. \( \sum_i V_i \bar{v}_i = 0. \)

\( v_i \) = partial molar volume of species \( i. \)

For a two component system (1) and (2), it can be shown

\[
\begin{align*}
\left( N \right)_2 &= - \left( N \right)_1 = N_1 \bar{v}_1 = N_2 \bar{v}_2 = - \frac{M}{M_1} \left( M \right)_2 = - \frac{M}{M_2} \left( M \right)_1 \\
\frac{V}{V_1} \left( V \right)_2 &= - \frac{V}{V_2} \left( V \right)_1. \\
\left( v \right)_1 &= 0; \left( v \right)_2 = 0. \\
\bar{M} &= N_1 M_1 + N_2 M_2 \\
\bar{V} &= N_1 V_1 + N_2 V_2
\end{align*}
\]

The results can be extended to multicomponent systems.

For additional amplification of these quantities and their use, references (67 - 71) will be of aid.
APPENDIX II

The validity of using normal chemical potentials in calculating the adsorption of an electrolyte at the liquid-air interface.

(Note: The basis for this argument is mainly contained in reference (69); Chapter 21).

The electrochemical potential of a charged species carrying a charge $Z_i$ can be written in the form

$$\bar{\mu}_i = \mu_i + Z_i F \phi$$  \hspace{1cm} (1)

where $\phi$ is the inner electrical potential at the point in the pure homogeneous phase under consideration (72), $Z_i$ is the number of charges carried by the ion $i$ and $F$ is the Faraday.

The chemical potential $\mu_i$ depends not only on temperature and concentration, but also on the electric field at the specified point. This is due to the fact that in an electric field molecules may be polarized or oriented, thus $\mu_i$ will be a function of field strength. Only in regions of constant inner electrical potential (i.e. when the electric field is zero), is $\mu_i$ the same as the normal chemical potential.

In considering the adsorption of electrolytes, at constant pressure the Gibbs Equation may be written as

$$-d\gamma = S^e \, dT + \sum_i \int d\bar{\mu}_i \hspace{1cm} (2)$$

where $S^e$ is the entropy per unit area $S/A$, including electrochemical effects and $\bar{\mu}_i$ is the electrochemical potential. For a pure homogeneous phase $\phi$ cannot vary, and this allows (2) to be written in terms of ordinary chemical potentials, for

$$\sum_i \int d\bar{\mu}_i = \sum_i \int d\mu_i + \sum_i Z_i \int dF \phi \hspace{1cm} (3)$$

Now $d\phi = 0$, hence

$$\sum_i \int d\bar{\mu}_i = \sum_i \int d\mu_i \hspace{1cm} (4)$$

Thus

$$d\gamma = -\sum_i \int d\mu_i \hspace{1cm} (5)$$
at constant temperature. This last equation can be applied to the adsorption of an electrolyte such as KCl at the liquid/liquid or liquid/air interface, particularly when one realizes that the Gibbs Convention results in the interface simply being regarded as a mathematical surface.
APPENDIX III

The treatment carried out here gives an alternative method of analysis of the pressure-area results. It is similar to that used by Sears (61) for stearic acid monolayers and is basically the same as that proposed by Guggenheim in his treatment of a two component system (73). The results arrived at are the same as in the first method illustrated in 5.4, but the path to them is more tortuous.

For the system $H_2O/ROH/KCl$ at the liquid air interface, one initially assumes $d\mu_{ROH} = 0$ (hence all terms involving $d\mu_{ROH}$ are zero). Following 5.1 - 5.4, one may write

$$-d\gamma = \int H_2O \, d\mu_{H_2O} + \int K^+ \, d\mu K^+ + \int Cl^- \, d\mu Cl^- \ldots \ldots \ldots (1)$$

Guggenheim (73) has shown that, in the liquid phase,

$$d\mu_i = -S_i dT + V_i dP + D\mu_i$$

where $D\mu_i = \frac{\partial \mu_i}{\partial x} dx$

If the mole fraction of KCl is $x$, then at constant temperature and assuming PV terms are small compared with RT in the liquid phase,

$$d\mu_{H_2O} = \frac{\partial H_2O}{\partial x} dx$$

$$d\mu K^+ = \frac{\partial K^+}{\partial x} dx$$

$$d\mu Cl^- = \frac{\partial Cl^-}{\partial x} dx$$

Substitution in (1) yields

$$-d\gamma = \left( \int H_2O \frac{\partial H_2O}{\partial x} + \int K^+ \frac{\partial K^+}{\partial x} + \int Cl^- \frac{\partial Cl^-}{\partial x} \right) dx \ldots \ldots \ldots (2)$$

The Gibbs-Duhem relation yields

$$(1 - x) \frac{d\mu_{H_2O}}{\partial x} + x \frac{d\mu K^+}{\partial x} + x \frac{d\mu Cl^-}{\partial x} = 0$$
\[ \frac{\partial H_2O}{\partial x} = -\left( \frac{x}{1-x} \right) \left[ \frac{\partial \mu K^+}{\partial x} + \frac{\partial \mu Cl^-}{\partial x} \right] \] ........................ (3)

Substituting (3) into (2) yields, noting that \[ K^+ = Cl^- = KCl, \]
\[ \frac{d\gamma}{dx} = \left[ -\left( \frac{x}{1-x} \right) \int H_2O + \int KCl \right] \left[ \frac{\partial K^+}{\partial x} + \frac{\partial Cl^-}{\partial x} \right] \] ........................ (4)

Since x is the only variable, \[ \frac{\partial \mu K^+}{\partial x} = \frac{d\mu K^+}{dx}; \frac{\partial \mu Cl^-}{\partial x} = \frac{d\mu Cl^-}{dx}; \]
\[ \partial x = dx. \]
Now \[ \mu K^+ = \mu K^+ + RT \ln (\lambda_+ x); \mu Cl^- = \mu Cl^- + RT \ln (\lambda_- x) \]
and \[ x_+ = x_- = x_{KCl}. \]

Assuming mole fraction activity coefficients = 1 (which is not valid
for concentrated KCl solutions, see 5.4 and below),
\[ -\frac{d\gamma}{dx} = \left[ -\left( \frac{x}{1-x} \right) \int H_2O + \int KCl \right] \left[ \frac{RT \ln (\lambda_{KCl})^2}{dx} \right] \]

Thus \[ -\frac{d\gamma}{dx} \frac{1}{2 RT} = \left[ -\left( \frac{x}{1-x} \right) \int H_2O + \int KCl \right] \frac{1}{x} \]
\[ = \frac{(1-x) \int KCl - x \int H_2O}{x(1-x)} \] ........................ (5)

If \[ x \ll 1, \text{ denominator becomes } \sim \int KCl \text{ (cf choosing } \int H_2O = 0) \]
Thus \[ -\frac{d\gamma}{dx} \frac{1}{2 RT} \sim \int \frac{KCl}{x} \] ........................ (6)

Note:
(1) Sears infers that KCl represents a total surface concentration.(61).
This is erroneous, as shown below.

(2) Equation (6) can be derived from (1) by choosing \[ \int H_2O = 0 \]
and assuming \[ Y_+ = 1. \]
i.e. \[ -\frac{d\gamma}{2 RT} = \int KCl \ln x \]}
thus \[ \frac{d\gamma}{dx} \times \frac{1}{2 RT} = \int \frac{(1)}{KCl} \]

\[ -\frac{1}{2} \frac{d\gamma}{d\mu_{KCl}} = \int KCl - \frac{x}{(1 - x)} \times \int H_{2}O \]

Neglecting the second term on the right hand side is not really justified since although \( x < 1, \int H_{2}O > \int KCl \)
i.e. \( \int KCl \) evaluated in this way is the same as assuming \( \int H_{2}O = 0 \) (refer to 5.4, Tables 5.5 and 5.6 for comparison between different \( KCl \)'s).
### APPENDIX IV

Surface Tension/\( \log_{10}(\xi^\pm M) \) DATA FOR NaCl, KCl and \( \text{NH}_4 \text{Cl} \) at 20°C. 

\( M \) = molality. 
\( \xi^\pm \) = mean ionic molal activity coefficient. 
\( \xi \) data from reference 51; \( \xi^\pm \) data from reference 74.

A. NaCl

<table>
<thead>
<tr>
<th>molality</th>
<th>0.1</th>
<th>0.25</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
<th>3.0</th>
<th>4.0</th>
<th>5.0</th>
<th>6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \xi )</td>
<td>72.9</td>
<td>73.2</td>
<td>73.6</td>
<td>74.4</td>
<td>76.0</td>
<td>77.7</td>
<td>79.3</td>
<td>80.9</td>
<td>82.6</td>
</tr>
<tr>
<td>( \xi^\pm )</td>
<td>.778</td>
<td>.717</td>
<td>.681</td>
<td>.657</td>
<td>.668</td>
<td>.714</td>
<td>.783</td>
<td>.874</td>
<td>.986</td>
</tr>
<tr>
<td>( \log_{10}(\xi^{\pm M}) )</td>
<td>-1.109</td>
<td>-1.747</td>
<td>-1.467</td>
<td>-1.182</td>
<td>+.126</td>
<td>+.331</td>
<td>+.496</td>
<td>+.641</td>
<td>+.772</td>
</tr>
</tbody>
</table>

B. KCl

<table>
<thead>
<tr>
<th>molality</th>
<th>0.1</th>
<th>0.25</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
<th>3.0</th>
<th>4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \xi )</td>
<td>72.9</td>
<td>73.1</td>
<td>73.5</td>
<td>74.2</td>
<td>75.5</td>
<td>77.9</td>
<td>78.3</td>
</tr>
<tr>
<td>( \xi^\pm )</td>
<td>.770</td>
<td>.703</td>
<td>.649</td>
<td>.604</td>
<td>.573</td>
<td>.569</td>
<td>.577</td>
</tr>
<tr>
<td>( \log_{10}(\xi^{\pm M}) )</td>
<td>-1.114</td>
<td>-1.755</td>
<td>-1.488</td>
<td>-1.219</td>
<td>+.059</td>
<td>+.232</td>
<td>+.363</td>
</tr>
</tbody>
</table>

C. \( \text{NH}_4 \text{Cl} \)

<table>
<thead>
<tr>
<th>molality</th>
<th>0.1</th>
<th>0.25</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
<th>3.0</th>
<th>4.0</th>
<th>5.0</th>
<th>6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \xi )</td>
<td>72.9</td>
<td>73.1</td>
<td>73.5</td>
<td>74.1</td>
<td>75.4</td>
<td>76.5</td>
<td>77.6</td>
<td>78.6</td>
<td>79.7</td>
</tr>
<tr>
<td>( \xi^\pm )</td>
<td>.770</td>
<td>.703</td>
<td>.649</td>
<td>.603</td>
<td>.570</td>
<td>.561</td>
<td>.560</td>
<td>.562</td>
<td>.564</td>
</tr>
<tr>
<td>( \log_{10}(\xi^{\pm M}) )</td>
<td>-1.114</td>
<td>-1.755</td>
<td>-1.488</td>
<td>-1.220</td>
<td>+.057</td>
<td>+.226</td>
<td>+.350</td>
<td>+.449</td>
<td>+.529</td>
</tr>
</tbody>
</table>

N. B. (1) Although the curves nearly superimpose, 
\[ \log_{10}(\xi^{\pm M}_{\text{NaCl}}) > \log_{10}(\xi^{\pm M}_{\text{KCl}}) > \log_{10}(\xi^{\pm M}_{\text{NH}_4 \text{Cl}}) \] at any given bulk molality, hence get different \( \xi^\pm \) i's.

(2) At concentrations \( \ll 0.5 \) molal, more accurate \( \xi / \xi^\pm \) data are required.
FIGURE I, APPENDIX IV

PLOT OF $\gamma$ VERSUS $\log_{10} (f + M)$ FOR VARIOUS SALTS AT 20°C

- NaCl
- KCl
- NH₄Cl

$\gamma$, dynes cm⁻¹

$\log_{10} (f + M)$
APPENDIX V

Tabulated data relating to the $\theta$ versus $\log_{10}(Y^+ \text{KCl})$ and $\log_{10} \chi$ plots (Figs. 4.7 to 4.11, Section 4.3; also see Section 5.4).

Mean ionic molar activity coefficients ($Y^+\text{KCl}$) were obtained from mean ionic molal activity coefficients ($\hat{f}^+$) by the following method.

$$Y^+ = \frac{M \cdot \text{do}}{C} \quad \ldots \quad (1) \quad \text{(ref. 126)}$$

where $C$ = molar concentration

$M$ = molal concentration

$\text{do}$ = density of solvent (water in this case).

At $21^\circ C$, $\text{do} = 1.003 \approx 1$

$$Y^+ \approx \frac{M \cdot \hat{f}^+}{C} \quad \ldots \quad (2)$$

Since $C$ was known, $M$ was computed from

$$M = \frac{C}{d - 0.001 C \cdot W_B} \quad \ldots \quad (3)$$

where $d$ = solution density

and $W_B$ = molecular weight of the solute.

Values of $d$ were obtained from reference 127, thus values of $M/C$ were calculated.

$\hat{f}^+$ values were obtained for KCl at $20^\circ C$ from references 74 and 128, hence the various $Y^+\text{KCl}$ quantities were evaluated. The surface tension of 2.5 and 3.5 molar KCl solutions was ascertained from the least squares relationship connecting $\theta$ and molarity shown in Figure 4.6. Refer to Table 1 below.
### TABLE I, APPENDIX V.
**SUMMARY OF DATA**

<table>
<thead>
<tr>
<th>Molar Concentration</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>2.5</th>
<th>3</th>
<th>3.5</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa^+$</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\gamma^-$</td>
<td>1</td>
<td>.604</td>
<td>.573</td>
<td>.573</td>
<td>.569</td>
<td>.571</td>
<td>.577</td>
</tr>
<tr>
<td>$\log_{10}(\gamma^- \cdot C_{KCl})$</td>
<td>-</td>
<td>-0.221</td>
<td>.084</td>
<td>.190</td>
<td>.274</td>
<td>.350</td>
<td>.437</td>
</tr>
<tr>
<td>$x$, mole fraction of KCl</td>
<td>0</td>
<td>.0177</td>
<td>.0348</td>
<td>.0430</td>
<td>.0512</td>
<td>.0592</td>
<td>.0670</td>
</tr>
<tr>
<td>Surface tension of monolayer free salt solution (dyne cm⁻¹)</td>
<td>72.6±1</td>
<td>74.2±.2</td>
<td>75.7±.2</td>
<td>76.1±.2</td>
<td>76.7±.2</td>
<td>77.2±.2</td>
<td>78.1±.2</td>
</tr>
<tr>
<td>$\Pi$ dyne cm⁻¹ at 21Å²</td>
<td>3.4±.5</td>
<td>4.4±.5</td>
<td>4.9±.5</td>
<td>4.6±.5</td>
<td>5.1±.5</td>
<td>5.1±.5</td>
<td>6.2±.5</td>
</tr>
<tr>
<td>$\gamma$ dyne cm⁻¹ at 21Å²</td>
<td>69.2±.6</td>
<td>69.8±.7</td>
<td>70.8±.7</td>
<td>71.5±.7</td>
<td>71.6±.7</td>
<td>72.1±.7</td>
<td>71.9±.7</td>
</tr>
<tr>
<td>$\Pi$ dyne cm⁻¹ at 20Å²</td>
<td>11.1±.5</td>
<td>11.6±.5</td>
<td>12.6±.5</td>
<td>12.5±.5</td>
<td>12.9±.5</td>
<td>12.9±.5</td>
<td>13.6±.6</td>
</tr>
<tr>
<td>$\gamma$ dyne cm⁻¹ at 20Å²</td>
<td>61.5±.6</td>
<td>62.6±.7</td>
<td>63.1±.7</td>
<td>63.6±.7</td>
<td>63.8±.7</td>
<td>64.3±.7</td>
<td>64.5±.7</td>
</tr>
<tr>
<td>$\Pi$ e dyne cm⁻¹ (area 19.0 – 19.3 Å²)</td>
<td>32.1±1</td>
<td>34.2±.3</td>
<td>35.6±.6</td>
<td>-</td>
<td>36.5±.5</td>
<td>-</td>
<td>38.4±.5</td>
</tr>
<tr>
<td>$\gamma$ e dyne cm⁻¹ (area 19.0 – 19.3 Å²)</td>
<td>40.5±.2</td>
<td>40.0±.5</td>
<td>40.1±.8</td>
<td>-</td>
<td>40.2±.7</td>
<td>-</td>
<td>39.7±.7</td>
</tr>
</tbody>
</table>

**Least Squares Analysis:**

- **Figure 4.6**  \( \gamma_o = 72.76 + 1.34 \cdot C_{KCl} \)  Error in slope: ±0.05
- **Figure 4.9**  \( \Pi_e = 32.38 + 1.49 \cdot C_{KCl} \)  Error in slope: ±0.10
- **Figure 4.10**  \( \gamma = 69.1 + 49 \cdot x \)
- **Figure 4.11**  \( \gamma = 61.6 + 44.6 \cdot x \)
APPENDIX VI

Summary of the $\pi - \alpha$ data relating to n-octadecanol on various substrates at 21°F. (see Figs. 4.1 to 4.5, Ch. 4)  $\alpha$ in $\alpha^2$, $\pi$ in dyne cm$^{-1}$.

1. PURE WATER AS SUBSTRATE

| $\alpha$ | 19.10 | 19.20 | 19.30 | 19.40 | 19.50 | 19.60 | 19.70 |
| $\pi$   | 42.5  | 38.0  | 33.5  | 29.3  | 25.3  | 21.0  | 17.0  |

| $\alpha$ | 19.80 | 19.90 | 20.00 | 20.25 | 20.50 | 20.75 | 21.00 |
| $\pi$   | 13.0  | 11.9  | 11.0  | 9.1   | 7.2   | 5.2   | 3.3   |

| $\alpha$ | 21.25 | 21.50 | 21.60 | 21.70 |
| $\pi$   | 1.8   | .6    | .2    | 0     |

2. 4M LiCl as substrate

| $\alpha$ | 18.38 | 18.58 | 18.77 | 18.97 | 19.20 | 19.36 | 19.55 |
| $\pi$   | 48.2  | 41.9  | 35.4  | 28.7  | 22.8  | 18.7  | 17.2  |

| $\alpha$ | 19.95 | 20.34 | 20.74 | 21.13 | 21.52 | 21.91 | 22.31 |
| $\pi$   | 14.5  | 11.9  | 8.9   | 6.5   | 4.1   | .23   | 1.0   |

| $\alpha$ | 22.70 |
| $\pi$   | .2    |

3. 4M NaCl AS SUBSTRATE

| $\alpha$ | 18.17 | 18.34 | 18.69 | 18.86 | 19.04 | 19.38 | 19.50 |
| $\pi$   | 48.5  | 44.1  | 35.0  | 30.3  | 26.8  | 19.9  | 18.0  |

| $\alpha$ | 19.73 | 20.08 | 20.43 | 20.78 | 21.47 | 21.80 | 22.17 |
| $\pi$   | 16.0  | 13.7  | 10.8  | 8.5   | 4.3   | 1.8   | .7    |

| $\alpha$ | 22.40 |
| $\pi$   | 0     |
### 4M KCl as Substrate

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ψ</td>
<td>41.3</td>
<td>34.7</td>
<td>28.8</td>
<td>21.7</td>
<td>15.9</td>
<td>15.1</td>
<td>14.5</td>
</tr>
<tr>
<td>A</td>
<td>20.10</td>
<td>20.48</td>
<td>20.86</td>
<td>21.24</td>
<td>21.62</td>
<td>22.0</td>
<td>22.2</td>
</tr>
<tr>
<td>Ψ</td>
<td>13.0</td>
<td>10.4</td>
<td>7.8</td>
<td>5.2</td>
<td>2.5</td>
<td>1.0</td>
<td>0.6</td>
</tr>
<tr>
<td>A</td>
<td>22.38</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ψ</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 5M KCl as Substrate

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ψ</td>
<td>41.8</td>
<td>34.5</td>
<td>27.6</td>
<td>20.7</td>
<td>15.2</td>
<td>13.2</td>
<td>10.7</td>
</tr>
<tr>
<td>A</td>
<td>20.37</td>
<td>20.57</td>
<td>20.75</td>
<td>20.96</td>
<td>21.20</td>
<td>21.36</td>
<td>21.74</td>
</tr>
<tr>
<td>Ψ</td>
<td>9.1</td>
<td>7.6</td>
<td>6.2</td>
<td>4.9</td>
<td>3.3</td>
<td>2.4</td>
<td>0</td>
</tr>
</tbody>
</table>

### 6M RbCl as Substrate

<table>
<thead>
<tr>
<th>A</th>
<th>18.15</th>
<th>18.44</th>
<th>18.83</th>
<th>19.00</th>
<th>19.22</th>
<th>19.40</th>
<th>19.61</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ψ</td>
<td>46.0</td>
<td>38.4</td>
<td>28.00</td>
<td>24.7</td>
<td>18.20</td>
<td>16.2</td>
<td>14.6</td>
</tr>
<tr>
<td>A</td>
<td>20.00</td>
<td>20.25</td>
<td>20.50</td>
<td>20.75</td>
<td>21.56</td>
<td>22.00</td>
<td>22.20</td>
</tr>
<tr>
<td>Ψ</td>
<td>11.9</td>
<td>10.5</td>
<td>8.7</td>
<td>7.2</td>
<td>2.2</td>
<td>0.8</td>
<td>0</td>
</tr>
</tbody>
</table>

### 7M CsCl as Substrate

<table>
<thead>
<tr>
<th>A</th>
<th>18.00</th>
<th>18.42</th>
<th>18.65</th>
<th>18.82</th>
<th>19.01</th>
<th>19.21</th>
<th>19.41</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ψ</td>
<td>50.7</td>
<td>40.6</td>
<td>35.0</td>
<td>30.2</td>
<td>25.1</td>
<td>20.9</td>
<td>17.4</td>
</tr>
<tr>
<td>A</td>
<td>19.61</td>
<td>19.80</td>
<td>20.00</td>
<td>20.20</td>
<td>20.40</td>
<td>20.79</td>
<td>21.00</td>
</tr>
<tr>
<td>Ψ</td>
<td>15.8</td>
<td>13.3</td>
<td>12.1</td>
<td>10.3</td>
<td>7.8</td>
<td>5.4</td>
<td>4.0</td>
</tr>
<tr>
<td>A</td>
<td>21.25</td>
<td>21.58</td>
<td>22.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ψ</td>
<td>2.6</td>
<td>1.0</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### 8. 4M NH₄Cl AS SUBSTRATE

<table>
<thead>
<tr>
<th></th>
<th>18.51</th>
<th>18.70</th>
<th>18.89</th>
<th>19.08</th>
<th>19.28</th>
<th>19.47</th>
<th>19.66</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>46.9</td>
<td>40.7</td>
<td>35.1</td>
<td>29.2</td>
<td>23.0</td>
<td>17.8</td>
<td>15.7</td>
</tr>
<tr>
<td>(g )</td>
<td>19.85</td>
<td>20.04</td>
<td>20.42</td>
<td>20.80</td>
<td>21.18</td>
<td>21.57</td>
<td>21.80</td>
</tr>
<tr>
<td>A</td>
<td>14.4</td>
<td>13.1</td>
<td>10.3</td>
<td>7.5</td>
<td>4.6</td>
<td>2.4</td>
<td>1.50</td>
</tr>
<tr>
<td>(g )</td>
<td>21.96</td>
<td>22.33</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 9. 4M \((\text{CH}_3)_4\text{N}^+\text{Cl}^-\) AS SUBSTRATE

<table>
<thead>
<tr>
<th></th>
<th>18.52</th>
<th>18.72</th>
<th>18.92</th>
<th>19.12</th>
<th>19.31</th>
<th>19.51</th>
<th>19.71</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>49.9</td>
<td>43.7</td>
<td>37.4</td>
<td>31.2</td>
<td>25.5</td>
<td>19.0</td>
<td>13.8</td>
</tr>
<tr>
<td>(g )</td>
<td>20.10</td>
<td>20.30</td>
<td>20.50</td>
<td>20.89</td>
<td>21.19</td>
<td>21.40</td>
<td>21.67</td>
</tr>
<tr>
<td>A</td>
<td>11.7</td>
<td>10.3</td>
<td>9.2</td>
<td>7.0</td>
<td>4.7</td>
<td>3.4</td>
<td>2.5</td>
</tr>
<tr>
<td>(g )</td>
<td>22.07</td>
<td>22.46</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 10. 4M MgCl₂ AS SUBSTRATE

<table>
<thead>
<tr>
<th></th>
<th>18.53</th>
<th>18.73</th>
<th>18.94</th>
<th>19.35</th>
<th>19.76</th>
<th>20.17</th>
<th>20.58</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>44.7</td>
<td>37.0</td>
<td>31.7</td>
<td>27.3</td>
<td>23.9</td>
<td>20.7</td>
<td>17.5</td>
</tr>
<tr>
<td>(g )</td>
<td>20.99</td>
<td>21.40</td>
<td>21.81</td>
<td>22.22</td>
<td>22.62</td>
<td>23.04</td>
<td>23.45</td>
</tr>
<tr>
<td>A</td>
<td>14.5</td>
<td>11.5</td>
<td>8.5</td>
<td>6.5</td>
<td>4.6</td>
<td>2.6</td>
<td>1.6</td>
</tr>
<tr>
<td>(g )</td>
<td>23.86</td>
<td>24.27</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0.9</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 11. 4M CaCl₂ AS SUBSTRATE

<table>
<thead>
<tr>
<th></th>
<th>18.04</th>
<th>18.24</th>
<th>18.44</th>
<th>18.65</th>
<th>19.06</th>
<th>19.47</th>
<th>19.88</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>44.4</td>
<td>40.0</td>
<td>34.7</td>
<td>29.8</td>
<td>24.7</td>
<td>21.9</td>
<td>19.0</td>
</tr>
<tr>
<td>(g )</td>
<td>20.29</td>
<td>20.70</td>
<td>21.52</td>
<td>21.95</td>
<td>22.34</td>
<td>22.75</td>
<td>23.16</td>
</tr>
<tr>
<td>A</td>
<td>16.2</td>
<td>13.3</td>
<td>8.0</td>
<td>5.4</td>
<td>3.7</td>
<td>2.0</td>
<td>0.9</td>
</tr>
<tr>
<td>(g )</td>
<td>23.57</td>
<td>23.57</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
REFERENCES.

1. J.C. Henniker
   Reviews of Mod. Physics 21 No 2 322 (1949)

2. B.V. Derjaguin et al
   Acta Physico chim URSS 19 541 (1944)

3. G. Karagounis

4. S. Levine
   Trans. Far Soc. 42B 102 (1946)

5. B.V. Derjaguin

6. E. Willis, G. Rennie, C. Smart, B.A. Pethica
   Nature 222 159 (1969)

7. E.R. Lippincott et al
   Science 164 1482 (1969)

8. Stig. R. Erlander

9. A. Cherkin
   Nature 224 1293 (1969)

10. W.W. Mansfield

11. Stig. R. Erlander
    Science 5A 60 (1969)

12. W. Drost-Hansen
    Ind. & Eng. Chem. 57 18 (1965)

13. " " "
    Advances in Chem. Series No. 67 70 (1967)

14. " " "
    Equilibrium Concepts in Natural Water Systems
    151st Meeting Amer. Chem. Soc. March 1965

15. " " "
    1st International Symposium on Water Desalination
    Oct. 3 - 9, 1965 (Washington)

16. " " "
    Ind. & Eng. Chem. 61 10 (1969)

17. " " " et al.
    J. Phys. Chem. 73 34 (1969)

18. G.J. Gittens

19. R. Cini, G. Loglio & A. Ficalbi
    Nature 223 1148 (1969)

20. J.R. O'Neil & L.H. Adami
    J. Phys. Chem. 73 1553 (1969)
<table>
<thead>
<tr>
<th></th>
<th>Author(s)</th>
<th>Journal/Book Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>G.L. Gaines</td>
<td>&quot;Insoluble Monolayers at Liquid-Gas Interfaces&quot; (Interscience 1966)</td>
</tr>
<tr>
<td>27</td>
<td>A.A. Trapeznikov</td>
<td>Acta phys. chim. URSS 20 589 (1945)</td>
</tr>
<tr>
<td>30</td>
<td>A. Roylance and T.G. Jones</td>
<td>J. Applied Chem 2 621 (1959)</td>
</tr>
<tr>
<td>31</td>
<td>J.J. Jasper</td>
<td>Record of Chemical Progress 26 169 (1965)</td>
</tr>
<tr>
<td>33</td>
<td>B.L. McConnell et al.</td>
<td>J. Phys. Chem. 68 2941 (1964)</td>
</tr>
<tr>
<td>36</td>
<td>M.J. Schick</td>
<td>J. Phys. Chem. 68 3585 (1964)</td>
</tr>
</tbody>
</table>
42. E.D. Goddard, Trans. Far Soc. 49 980 (1953)
44. Ira Weil, J. Phys. Chem. 70 133 (1966)
51. International Critical Tables, 4 p. 463 - 466
52. Landolt Bornstein, 6th Edn. Band 2; p 444 Table 23/1215 Teil 3;
54. I. Langmuir, Science 88 450 (1938)
60. H. Lange, in "Non-Ionic Surfactants" ed. M. Schick (Marcel Dekker, 1968)
<table>
<thead>
<tr>
<th>Page</th>
<th>Author(s)</th>
<th>Journal/Title</th>
<th>Volume</th>
<th>Issue</th>
<th>Pages</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>63.</td>
<td>F.A. Long and W.F. McDevitt</td>
<td>Chem. Revs.</td>
<td>51</td>
<td></td>
<td>119</td>
<td>1952</td>
</tr>
<tr>
<td>64.</td>
<td>G. Akerlof</td>
<td>J. Am. Chem. Soc.</td>
<td>51</td>
<td></td>
<td>984</td>
<td>1929</td>
</tr>
<tr>
<td>67.</td>
<td>E.A. Guggenheim</td>
<td>Trans. Far Soc.</td>
<td>36</td>
<td></td>
<td>397</td>
<td>1940</td>
</tr>
<tr>
<td>70.</td>
<td>J.L. Moilliet, B. Collie and W. Black</td>
<td>&quot;Surface Activity&quot;</td>
<td>(van Nostrand 1961)</td>
<td>Ch. 3.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>73.</td>
<td>E.A. Guggenheim</td>
<td>&quot;Thermodynamics&quot;</td>
<td>(North Holland 1957)</td>
<td>3rd edn.</td>
<td>Ch. 5.</td>
<td></td>
</tr>
<tr>
<td>75.</td>
<td>M. Falk and G.S. Kell</td>
<td>Science</td>
<td>154</td>
<td></td>
<td>1013</td>
<td>1966</td>
</tr>
</tbody>
</table>
79. H.M. Chadwell  Chem. Reviews 4 375 (1927)
82. E. Forslind  Acta Polytech. Scand. 115 3 (1952)
84. H.S. Frank and W.Y. Wen  Disc. Far. Soc. 24 133 (1957)
88. G. Jones & M. Dole  J. Amer. Chem. Soc. 51 2950 (1929)
90. R.W. Gurney  "Ionic Processes in Solution" (McGraw-Hill 1953)
96. R.J. Good  J. Phys. Chem. 61 810 (1957)
103. M. Blank & V.K. La Mer  Proc. 2nd International Congress on Surface Activity (1957)
104. " " " "  J. Phys. Chem. 61 1611 (1957)
105. V.K. LaMer & M. Blank  J. Coll Sci. 11 608 (1956)
111. J.F. Danielli & E.N. Harvey  J. Cellular Comp. Physiol. 5 483 (1935)
114. G. Ling  Science 155 301 (1967)
115. H.N. Christensen  "Biological Transport" (Benjamin 1962)
112.


122. V.K. La Mer  in "Retardation of Evaporation by Monolayers" ed. (La Mer) Academic Press N.Y. (1962)

123. D.G. Kolp & E.S. Lutton  J. Am. Chem. Soc. 73 5593 (1951)


128. B.E. Conway  "Electrochemical Data" Chapter III Elsevier (1952)

129. V.K. La Mer & T.W. Healy  Proceedings of the National Academy of Sciences 52 679 (1964)


113.


135. V.K. La Mer & T.W. Healy  Science 148 36 (1965)