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**Adsorption of surfactants at solid/liquid and liquid/liquid
interfaces for dewetting process**

Chan, Steven Yick-Yuen, Ph.D.

City University of New York, 1988

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**ADSORPTION OF SURFACTANTS AT SOLID/LIQUID
AND LIQUID/LIQUID INTERFACES
FOR DEWETTING PROCESS**

by

Steven Yick-Yuen Chan

**A dissertation submitted to the Graduate Faculty in
Engineering in partial fulfillment of the
requirements for the degree of Doctor of Philosophy,
The City University of New York.**

1988

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1988

This manuscript has been read and accepted for the Graduate Faculty in Engineering in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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Abstract

ADSORPTION OF SURFACTANTS AT SOLID/LIQUID AND LIQUID/LIQUID INTERFACES FOR DEWETTING PROCESS

by

Steven Yick-Yuen Chan

Advisor : Professor Henri L. Rosano

Dewetting is an industrial drying process by adsorption of surfactants at the solid/liquid interface. From dewetting tests, it was found that glass, with a highly negative charged surface, is dewetted instantaneously by cationic surfactants while less charged surface takes longer time or may not be dewetted at all. This implies that electrostatic forces play an important role in adsorption and it was studied by electrocapillarity using mercury as the model solid. Interfacial tensions were calculated from measured drop times versus the applied potential using a modified Regula Falsi computer program. Amphoteric surfactant, Sarkosyl O, adsorbs at the dropping mercury electrode at moderate cathodic and anodic potentials only. At more extreme potentials, there is an increase in competition from the much more prevalent water dipoles and the coulombically attracted supporting electrolyte, eventually displacing the surfactant. Anionic surfactant, Aerosol OT, starts being adsorbed at moderate cathodic potential. After reaching a maximum at around the point of zero charge, adsorption remains relatively constant as the potential is increased in the anodic branch. Desorption does not occur as in the case of the amphoteric surfactant because the coulombic attractive forces of the anionic surfactant and the supporting electrolyte are equal in magnitude. Cationic surfactant, Didodecyltrimethylammonium Nitrate, behaves unexpectedly

when compared to Aerosol OT as the interfacial pressure decreases back to zero in the extreme cathodic branch. Detailed study of a homologous series of quaternary ammonium surfactants shows condensed liquid film and solid film are formed at the interface. Further study of the cationic surfactant using Surface Enhanced Raman Scattering technique shows that maximum intensity for peaks of the CH_2 stretches and scissoring were found at high negative potential. All these results indicate that cationic surfactants interact so strongly with negatively charged surfaces that the polar head group of the surfactant loses its lateral repulsion. At high negative potential, the formation of the surfactant monolayer (solid type) at the interface accounts for the decrease in interfacial pressure in electrocapillary experiment.

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Thanks also go to my parents, Mr. and Mrs. K.P.Chan. It was love that made them decide to immigrate into United States, a completely new country for them so that their children had the opportunity to continue their higher education.

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CHAPTER 1

INTRODUCTORY REMARK

1.1. INTRODUCTION OF DEWETTING

Water removal from solids is an important manufacturing step in the metal finishing and assembly industries. Common methods include evaporation, centrifugation, and absorption. However, they all have a disadvantage in one way or another. There is a need for rapid and efficient drying of a variety of non-absorbent materials. For example, silicon wafers, copper and glass components used in miniaturized electronic circuit need to be dried quickly and thoroughly to avoid the formation of dry stains on the surface of such materials. Such stains comprise water-soluble materials which would adversely affect the electrical properties of the materials. In addition, certain metal parts, and particularly precision metal parts, must be completely dry before they are assembled. As in the case of ball needle and roller bearing, if inserted in a race while wet they will corrode and freeze the bearing assemble. Accordingly, it is necessary that many metal parts be completely dried immediately after the machining or cleaning operation before they can be assembled.

The oldest and simplest method of drying water-wet solids is by evaporative drying. In many machining and cleaning operations, metal parts have to be into contact with water. Many machined metals, such as bearings and precision valve components cannot tolerate corrosion because of the fine tolerances that are usually required and because water tends to lead to much more rapid corrosion of these metal surfaces. The evaporative method is unsuitable for drying solids made from important metals, such as ferrous metals. Rusting and corrosion will take place if water is allowed to evaporate from their surface at high temperature, particularly if the surface is free of protective materials. Evaporative drying of

decorative materials leaves objectionable water spots resulting from the deposition of water-soluble soils as water evaporates. Since many water-soluble materials are electrolytes, that can result in electrical conductivity and induced voltaic effects. Therefore, these spots are especially undesirable in the case of electrical and electronic equipments. Also, high temperature operation is not suitable for heat sensitive solids such as plastic materials. Moreover, heating requires special handling which is undesirable. In addition, this method requires large amounts of energy to operate : as approximately 1,000 Btu are needed to evaporate one pound of water.

The centrifugal method is effective only in removing gross amounts of water from free draining materials. It leaves a film of water on the solid. Another method has to be used after the centrifuge for complete water removal.

Absorption requires large amounts of absorbent, such as sawdust or corn-cobs which then must be disposed of or dried. Furthermore, the solids must then be further processed to remove residue deposited by the drying absorbent.

The new method in drying is solvent drying which can offer one-step, low energy and spot-free drying. Solvent drying can be done by :

- 1) *dissolving the water* with flammable polar solvent, such as alcohol or acetone. The solvent will dissolve the water on the solid and evaporate fast because of the low boiling point. Nevertheless, polar solvents are explosive and dangerous to use. Special equipment and precautions must be taken. Also, the solvent has to be recovered by methods such as distillation or extraction, which are expensive.
- 2) *Displacing the water* by an immiscible solvent containing surfactant(s). Displaced water is separated simply by density difference. The immiscible solvent is then allowed to evaporate from the solid surface instead of water. Therefore, corrosion and rusting will not occur. Water

soluble materials will remain in the water phase so that no spots will be formed as the solvent is evaporated. Detail of this process will be discussed later.

It is the latest method that was interesting to this research, whose aim is to investigate the mechanism and the main factors involved in the water displacement by a fluorocarbon/surfactant(s) solvent. Following this reasoning, it is necessary to understand :

- 1) the physical and chemical properties of the fluorocarbon,
- 2) interaction of surfactants,
- 3) the adsorption mechanism of surfactant at solid/water/fluorocarbon interfaces.

1.2. BACKGROUND

1.2.1. DEWETTING BY DISPLACEMENT

The proposed mechanism of dewetting by a fluorocarbon surfactant solution is illustrated in Figure 1.1. Water is removed from the solid surface by immersing the wet solid into a fluorocarbon oil containing surfactant. Upon adsorption of the surfactant onto the solid surface, water is displaced and it rises to the surface of the fluorocarbon oil due to density difference.

When the solid is wettable by water in air, the tensions at the 3-phase contact line are γ_w , γ_s , $\gamma_{w/s}$ as shown in Figure 1.2, where the γ 's are surface tensions of water and solid and interfacial tension of water/solid respectively. According to Young's Equation (1) at equilibrium :

$$\gamma_s = \gamma_w \cos \theta + \gamma_{w/s} \quad (1.1)$$

Usually, wetting means that the contact angle, θ is zero or so close to zero that water spreads over the solid. If the angle is zero, Equation (1.1) ceases to hold and the imbalance of the tensions is given by Dupre's Equation (2) :

$$S = \gamma_s - \gamma_w - \gamma_{w/s} \quad (1.2)$$

where S is known as the spreading coefficient. When S is positive, water will wet the surface or vice versa.

The same treatment can be done to a solid-liquid-liquid system where two mutually immiscible liquids are involved as shown in Figure 1.2. Young's Equation now becomes :

$$\gamma_{s/o} = \gamma_{w/o} \cos \theta + \gamma_{w/s} \quad (1.3)$$

or

$$\cos \theta = \frac{\gamma_{s/o} - \gamma_{w/s}}{\gamma_{w/o}} \quad (1.4)$$

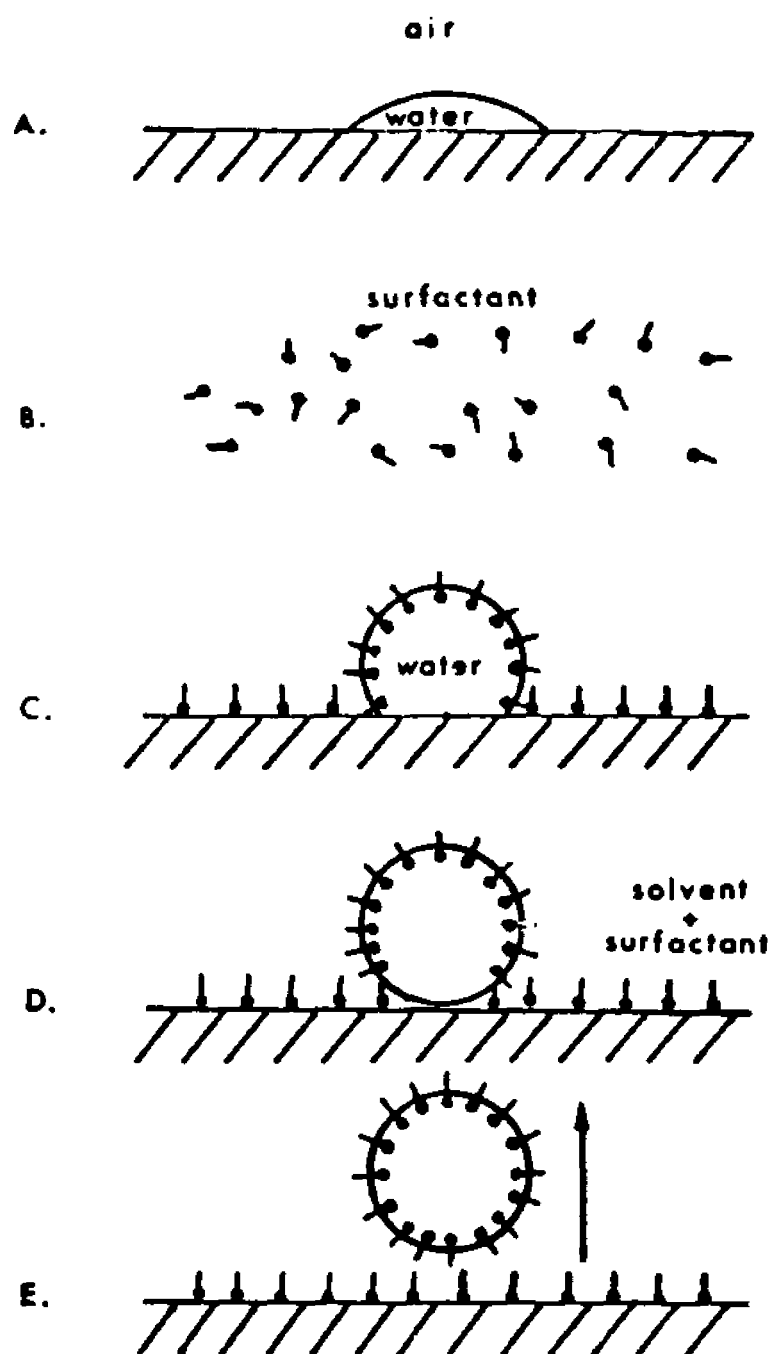


Figure 1.1 Mechanism of dewetting of a solid surface by fluorocarbon surfactant solution

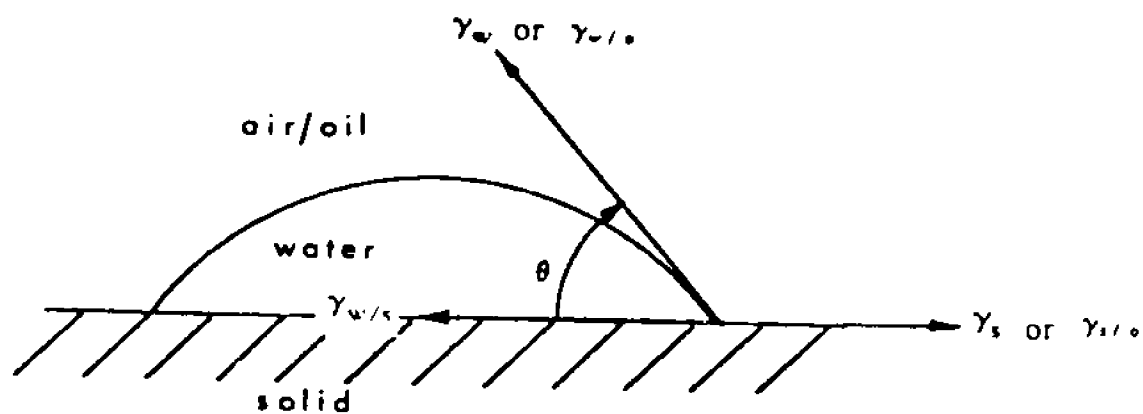


Figure 1.2 Tensions at solid/water/air (oil) contact line

where $\gamma_{s/o}$ = interfacial tension of solid/oil

$\gamma_{w/o}$ = interfacial tension of water/oil

$\gamma_{w/s}$ = interfacial tension of water/solid

θ = contact angle

In order to dewet the solid, one would like to increase the contact angle, in other words, to decrease the value of $\cos \theta$ as much as possible. This can be achieved by adsorption of the surfactant at the solid/oil and water/oil interfaces as in Figure 1.1 where a simple mechanism of dewetting is shown. Since $\gamma_{s/o}$ is lowered by adsorption of surfactant while $\gamma_{w/s}$ remains constant, θ will increase. If lowering of $\gamma_{s/o}$ is high enough, i.e., smaller than $\gamma_{w/s}$, dewetting will occur as $\gamma_{w/o}$ is usually lowered to a very small value. Given that $\gamma_{w/o}$ is close to zero, dewetting will be spontaneous. Therefore, the criteria of dewetting for the solid-water-oil system is :

$$\gamma_{w/s} > \gamma_{s/o} - \gamma_{w/o} \cos \theta \quad (1.5)$$

It also has to be mentioned that when the contact angle is larger than 90° , $\cos \theta$ becomes negative. For dewetting, θ has to close to 180° , or $\cos \theta$ is equal to -1. This allow us to rewrite equation (1.5) as :

$$\gamma_{w/s} > \gamma_{s/o} + \gamma_{w/o} \quad (1.6)$$

Defining the dewetting coefficient, D in the manner as the spreading coefficient as :

$$D = \gamma_{w/s} - \gamma_{s/o} - \gamma_{w/o} = -(S + 2\gamma_{w/o}) \quad (1.7)$$

dewetting will occur when D is positive. It is only when D or S are less than zero but larger than $-2\gamma_{w/o}$, that a finite contact angle will be formed.

1.2.2. SOLVENTS

1.2.2.1. Specifications Of Solvent And Surfactant

- 1) low boiling point of solvent, at about 50°C for low consumption of heat
- 2) solvent should be of high density, at least 1.3g/cc at 20°C for fast separation with water
- 3) solvent must be immiscible with water
- 4) fast aqueous emulsion separation time preferably not more than five minutes
- 5) solvent must not be flammable nor explosive
- 6) solvent should not form an azeotrope containing more than 4% of water, nor boil at more than 4°C below the boiling point of the solvent
- 7) the solvent should be chemically unreactive
- 8) solvent with dissolved surfactant should have low interfacial tension versus water, less than 5 dynes/cm
- 9) low surfactant concentration required, about 0.1 to 2.5 g/l
- 10) surfactant should not be extractable by water

The common solvent that satisfies the above specifications is trifluoro- trichloro ethane.

1.2.2.2. Commercial Solutions

- 1) Dupont "Freon" T-DFC solvent, Bullet No. FS-19C Dupont de Nemours and U.S. Patent No. 4182687 by P.L.Bartlett (3)

Surfactants under this patent are a combination of cationic and anionic surfactants. The preferred combination seems to be a long chain tetra-alkyl ammonium compound (cationic) and a long chain phosphate esters (anionic).

2) Allied Chemical "Genesolv DRM"

The surfactant used by Allied Chemical is an oleoyl sarcosine which is a modified fatty acid interrupted by an amidomethyl ($-\text{CONCH}_3-$) group (ampho-
teric).

1.2.3. COMMERCIAL DEWETTING EQUIPMENT

The common configuration of the drying equipment (4-7) is illustrated in Figure 1.3. It contains an immersion sump connected to an ultrasonic generator. After short immersion in the solvent, water on wet parts of the solids agglomerates and rises to the surface of the heavier solvent. Then, the separated water, along with some solvent, is driven from the surface into a gravity water-solvent separator. The solids are then removed and passed through one or more baths. Or, they remain in a vapor zone as fresh solvent is sprayed to remove any water residue or adsorbed surfactant. These completely clean and dried solids are then removed.

The solvent is fed to the water separator in the form of a distillate from a condensing coil, water/solvent mixture from the immersion sump and excess from the boil sump. Cooling coils are usually used to reduce the solubility of water in the solvent. Water is separated by gravity from the solvent. The separated water is drained while the water-free solvent is passed under and over dams into the reservoir. Further cooling may be required in the reservoir and the solvent is directed to the recirculating pump.

From the reservoir, the water-free solvent is pumped to the boil sump for makeup and also through a low-micron filter to the immersion sump and the spray lance. Upon entering the boil sump, the solvent is boiled in the boil sump to

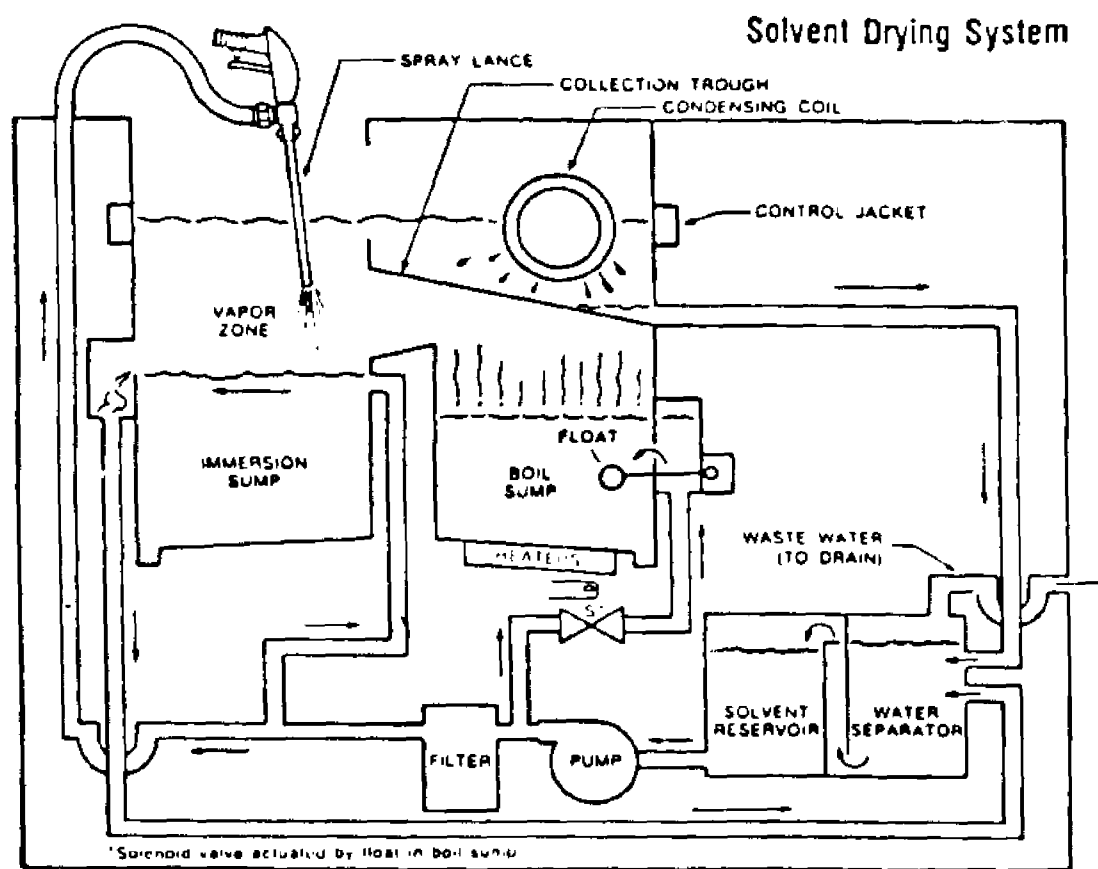


Figure 1.3 Commercial equipment for dewetting of solids

create a dense vapor which rises and fills the vapor zone. Vapor is condensed on the condensing coil. The distillate is collected and flows back to the separator. The solvent which enters the immersion sump through a sparger chamber, creates a skimming action and sweeps the water that has been removed from the solids over a weir and back to the water separator.

The cycle provides a continuous supply of clean water-free solvent to the immersion sump, vapor for spot-free drying and rejection of separated water from the system. As no water evaporates from the wet solids at this low temperature, water soluble compounds cannot be deposited on the solid surface.

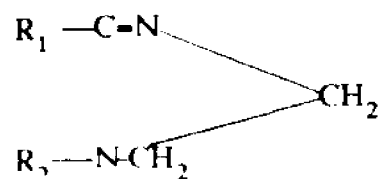
1.3. LITERATURE REVIEW

1.3.1. DEWETTING

Numerous authors patented formulations for both solvents and surfactants for water displacement (8-22). Most of the patents used trifluoro-trichloro-ethane as the solvent which could satisfy the specifications for the purpose of water displacement. To be more specific, the fluoro-chloro-carbon is 1,1,2-trichloro-1,2,2-trifluoroethane. It boils at 48°C (at 760 mm Hg) , with a specific density of 1.57 at 20°C and low latent heat of 35 cal/g. It is not chemically reactive nor explosive. All these physical properties make it suitable as the water displacement solvent. Usually, an azeotrope mixture of the above mentioned fluorocarbon and a short chain alcohol, i.e. methanol, ethanol and isopropanol, is used instead of the pure fluorocarbon oil. The addition of the alcohol is to increase the polarity of the fluorocarbon which is only slightly polar. This will then increase the solubility of charged and high molecular weight surfactants in the solvent while the physical properties do not change by much. For example, isopropanol and the trichloro-trifluoro-ethane form an azeotrope at 3% alcohol and 97% oil (by weight). This mixture boils at 46.5°C and has a specific density of 1.53 at 20°C.

In the patents mentioned, wide varieties of surfactants were used : cationic, anionic, amphoteric, and non-ionic. Since certain surfactants tend to be adsorbed by certain solids specifically, one surfactant may dewet one particular solid but not others. Dupont owns many patents using combinations of cationic and anionic surfactants. The cation is a tetra-alkyl ammonium compound which is probably the most common commercial cationic surfactant. Saturated aliphatic amines were also used (10,11) to neutralize the anionic surfactants. Choice of anion varies as many different kinds of anionic surfactants are available. Steinacker (10) and Burt (11) used alkyl phosphate ester and oxo-phostates. Brandreth (13) tried other fluorocarbon oils and selected the cationic surfactant as imidazoline

moieties.



Bartlett (3) experimented with dialkyl-dimethyl ammonium compound with many anionic surfactants consisting of different head groups as carboxylic, sulfonate, sulfate and phosphate.

The combination of anionic and cationic surfactants seems to work better than amphoteric and non-ionic surfactants. This is because beside the structural effect of the solid and surfactant, the electrical properties play an important role in adsorption. It makes sense that cationic surfactants adsorb onto negative charged solid surfaces and anionic onto positive ones. It is well known that cationic and anionic surfactants form an association which is more surface active than the individual surfactants. This bulky association makes it more oil soluble so that it tends to stay in the oil phase and is harder to extract by water. However, this association is not strong enough in fluorocarbon as it probably splits and adsorbs onto the opposite charged solid surface.

In order to understand the mechanism of dewetting, it is necessary to review some electrical properties of a solid/liquid interface.

1.3.2. ELECTRICAL PROPERTIES OF A SOLID/LIQUID INTERFACE

1.3.2.1. ELECTRICAL DOUBLE LAYER

Across any interface separating two phases, there is, in general, a difference in potential since the electrical environment of a test charge changes as it is carried from one phase to the other.

The potential difference across an interface, since electricity is atomic in nature, may conveniently be pictured as an *electrical double layer*. One phase acquires a net negative charge (excess of electrons), and the other a net positive charge (deficiency of electrons).

The first quantitative discussion of this double layer was given in 1879 by Helmholtz (23a), who considered the case of a solid immersed in a solution. He suggested the picture shown in Figure 1.4, a layer of ions at the solid surface and a rigidly held layer of oppositely charged ions in the solution. These two sheets of charge, having opposite polarity, are separated by a distance of molecular order. The electrical potential, ψ , corresponding to such a charged distribution is also shown.

The Helmholtz double layer is equivalent to a simple parallel-plate capacitor. If l is the distance separating the oppositely charged plates and ϵ , the dielectric constant of the medium, the capacitance per square centimeter of the interface is $\epsilon/4\pi l$. If Q/A is the surface charge density (e.g., coulombs per cm^2) the potential ΔU across the double layer is :

$$\Delta U = \frac{4 \pi l Q}{\epsilon A} \quad (18)$$

However, the Helmholtz model of the double layer is inadequate because thermal motions of the liquid molecules could scarcely permit such a rigid array of charges at the interface. The *diffuse double layer*, proposed by Gouy (23) and

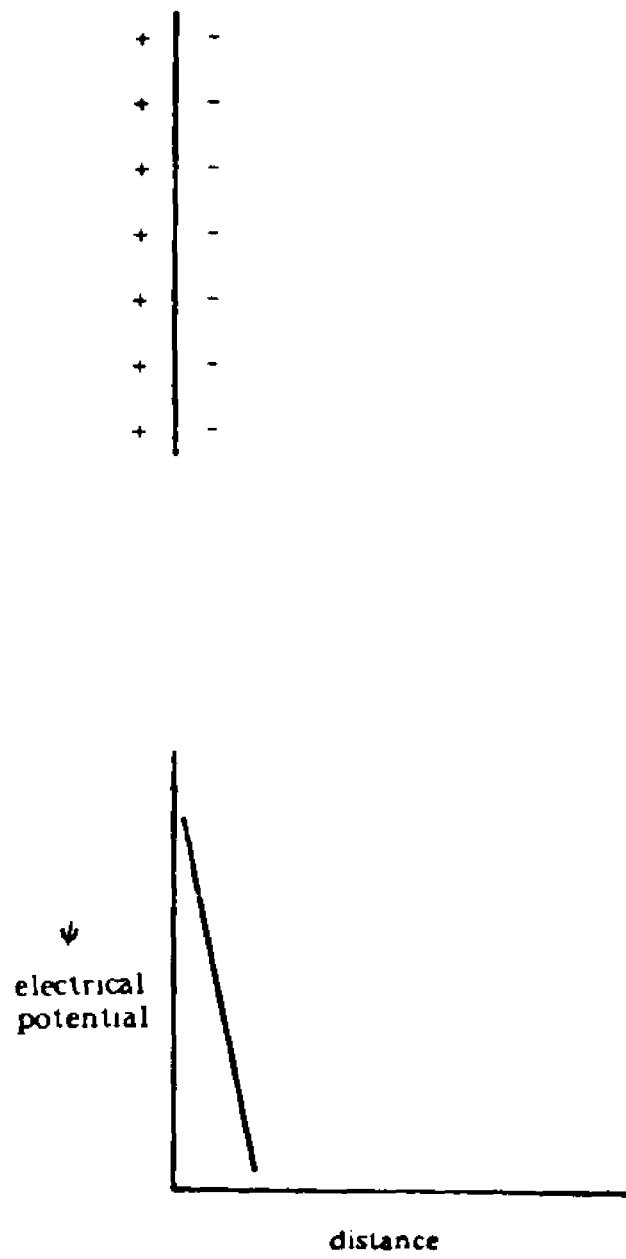


Figure 1.4 Helmholtz double layer

independently by Chapman (24) seems to be more realistic. This is shown in Figures 1.5 and 1.6. The charge on the solid is rigidly fixed. Adsorbed on the top of this, there may be a partially immobile layer of oppositely charged molecules of liquid. Further, in the solution there is a diffuse layer of charge, which may have either the same sign as or opposite from that of the adsorbed layer. Only this diffuse region is free to move under the influence of an applied potential difference. The electrical potential, ψ in this case is :

$$e^{\frac{y}{2}} = \frac{e^{\frac{y_0}{2}} + 1 + (e^{\frac{y_0}{2}} - 1)e^{-\kappa x}}{e^{\frac{y_0}{2}} + 1 - (e^{\frac{y_0}{2}} - 1)e^{-\kappa x}} \quad (1.9)$$

where $y = \frac{z e \psi}{k T}$

$$y_0 = \frac{z e \psi_0}{k T}$$

ψ_0 = electrical potential at the surface

z = valence of the ion

e = charge on the electron

k = Boltzmann's constant

T = absolute temperature

$$\kappa^2 = \frac{4 \pi e^2}{\epsilon k T} \sum_i n_i z_i^2$$

ϵ = dielectric constant of the medium

n = concentration of ions

When $y_0 \ll 1$, or for single charged ions at room temperature, $\psi_0 \ll 25$, equation (1.9) is approximated by Dybe-Hickel (25) as :

$$\psi = \psi_0 e^{-\kappa x} \quad (1.10)$$

The quantity $1/\kappa$ is thus the distance at which the potential has reached the $1/e$ fraction of its value at the surface and coincides with the center of action of the space charge. The plane at $x = 1/\kappa$ is therefore taken as the effective thickness of the diffuse double layer.

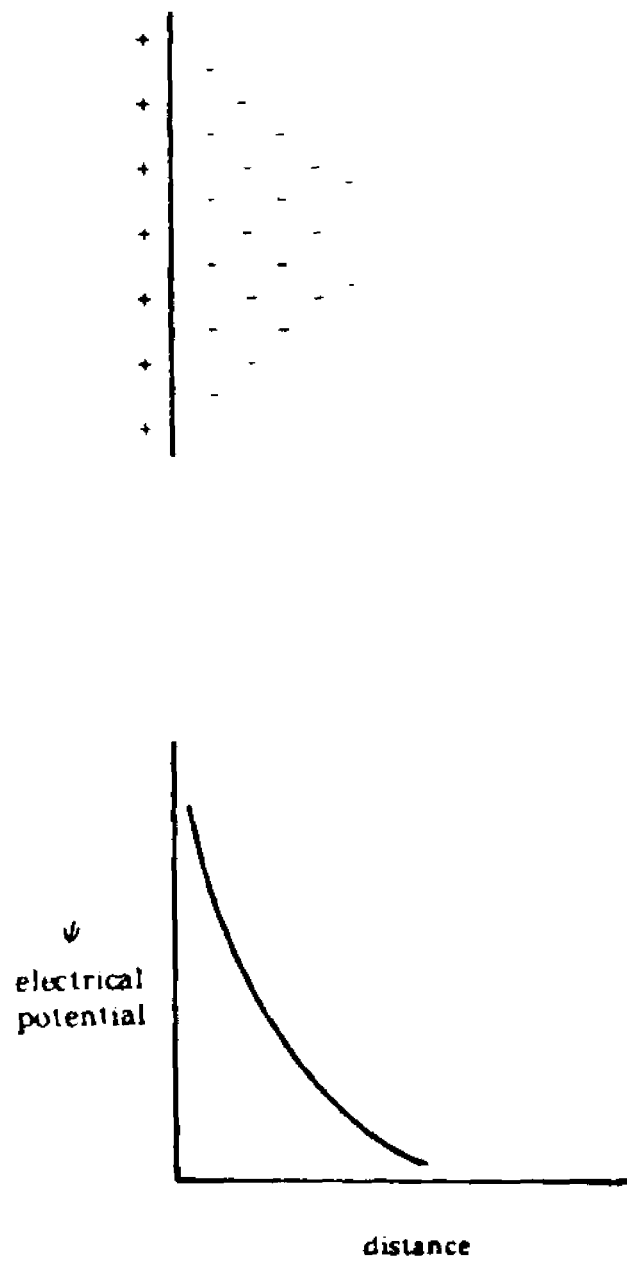


Figure 1.5 Diffuse double layer

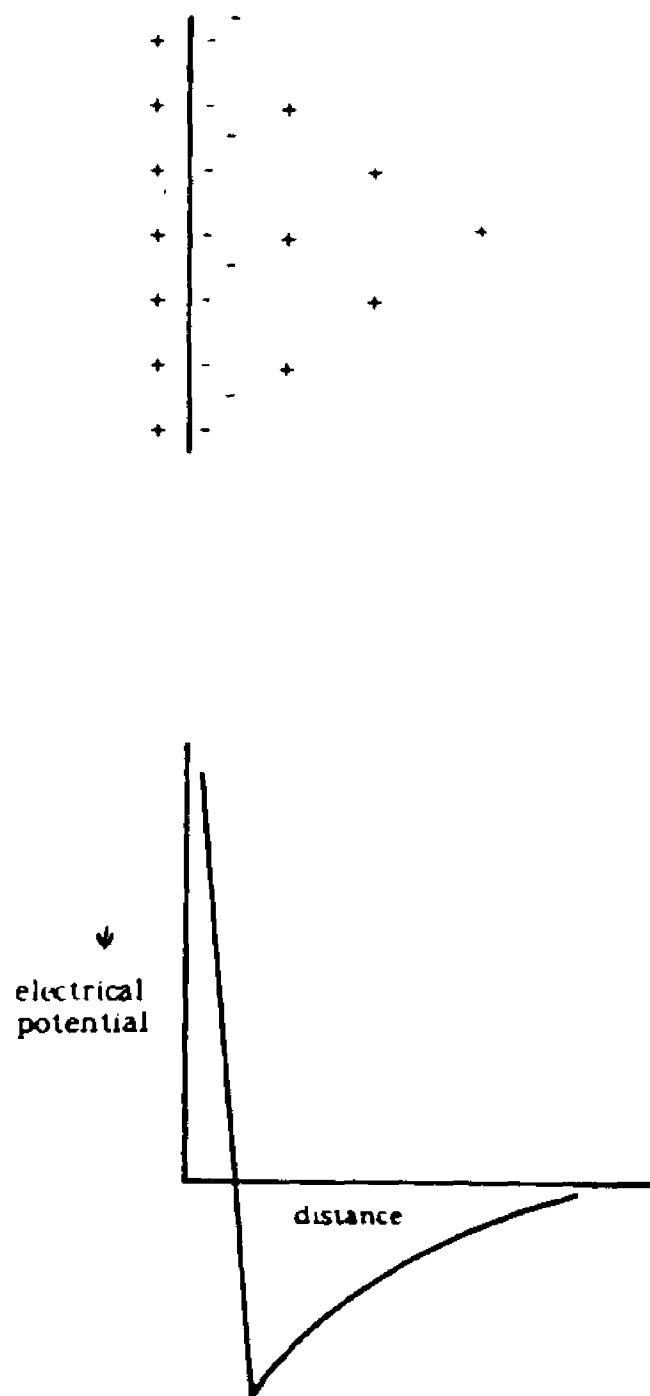


Figure 1.6 Diffuse double layer with reversal of sign

For $y_0 \gg 1$ and $x \gg 1/\kappa$, equation (9) becomes :

$$\psi = \frac{4 k T}{z e} e^{-\kappa x} \quad (1.11)$$

This shows that the potential at some distance away from the interface follows equation (1.8) but with an apparent ψ_0 value of $4 k T / z e$. This apparent ψ_0 is independent of the actual value of ψ_0 .

The surface charge density, σ can also be calculated by :

$$\sigma = - \int_0^{\infty} \rho \, dx \quad (1.12)$$

or,

$$\sigma = - \frac{\epsilon}{4 \pi} \int_0^{\infty} \frac{d^2 \psi}{dx^2} \, dx \quad (1.13)$$

where ρ is the net charge density at any point.

Upon integration,

$$\sigma = - \left[\frac{\epsilon}{4 \pi} \right] \left[\frac{d \psi}{dx} \right]_{x=0}^{\infty} \quad (1.14)$$

From equation (9)

$$\sigma = \left[\frac{2 n_0 \epsilon k T}{\pi} \right]^{1/2} \sinh \frac{y_0}{2} \quad (1.15)$$

Or using Dyke-Hickel approximation :

$$\sigma = \frac{\epsilon \kappa \psi_0}{4 \pi} \quad (1.16)$$

The Gouy-Chapman treatment of double layer does not hold at small κx values when ψ_0 is large. This is due to the assumption of point charges and the consequent neglect of ionic diameters. Stern (26) handled it by dividing the region near the interface into two parts. The first consists of a layer of ions adsorbed at the interface and forms the inner, compact double layer. The second or the outer one is the diffuse Gouy-Chapman layer. If the thickness of the

compact layer is δ , σ_s is :

$$\sigma_s = \frac{\epsilon'}{4\pi\delta} \left| \psi_0 - \psi_\delta \right| \quad (1.17)$$

The total surface charge density is the sum of σ_s and σ_d for the two layers and the total electrical capacity is given by :

$$\frac{1}{C} = \frac{1}{C_s} + \frac{1}{C_d} \quad (1.18)$$

for capacity in series. At high concentration, C_d becomes sufficiently large such that C can be approximated as C_s .

1.3.2.2. ELECTROKINETIC PHENOMENA AND ZETA POTENTIAL

Electrokinetic phenomena means that the phenomena involves electricity and is connected with the tangential movement of two phases along each other. They may arise either from an external electric field directed along the phase boundary and resulting in a movement, or from a movement of the phase boundary directly resulting in a transport of electricity. Examples of the first kind are electro-osmosis and electrophoresis, and of the second kind, streaming potential and migration potential.

In all modes of calculation, the electrical potential at the slipping-plane between the fixed and the moving liquid is called the *zeta potential* (ζ). The zeta potential is not strictly a phase-boundary potential because it is developed wholly within the field region. It can be regarded as the potential difference in an otherwise practically uniform medium between a point some distance from the interface and a point on the plane of shear.

Electrolytes (Aluminum salts, Thorium salts, crystal violet, etc.) strongly influence the zeta potential but have no effect on the total potential drop. The

reversal of ζ as in Figure 1.6 is caused by a strong adsorbability of ions in question or of the products of their hydrolysis. The adsorbed layer must bear a larger charge than is present on the wall, so that in the outer part of the double layer, the charge and the potential must be reversed in order to maintain electro-neutrality.

ζ potential of metals have been investigated mainly by electrophoresis. Generally, metals are negative with respect to water. Probably, all metals are covered by a layer of chemically adsorbed oxygen. The electrons of the metal-oxygen bonds are displaced to the oxygen which give rise to a dipole layer and may be seen as the cause of the negative zeta potential (27).

1.3.3. ADSORPTION OF SURFACTANT AT INTERFACES

It is well known that surfactants tend to be adsorbed at the interfaces. Hansen (28) developed interfacial excess quantity in evaluation of the thermodynamic quantities of adsorption at a plane interface. Also, partial derivatives of interfacial tension with respect to independent intensive variables were developed to determine the interfacial densities of surface active substances and the changes of entropy and volume associated with the adsorption. Motomura and his co-authors (29) studied adsorption at interfaces and introduced the mean partial molar thermodynamic quantity in the interface and showed the procedure to estimate those quantities to different systems. For the system of water and dilute solution of tetradecanol in hexane, it was observed that the thermodynamic quantities of interface formation decreases, while the interfacial concentration increases with the increase of the mole fraction of tetradecanol. Results are explained in terms of negative values of the partial molar quantity changes. In the case of

aqueous solution of sodium dodecyl sulfate (SDS) and hexane, the surfactant has a negative entropy of interface formation which is smaller than tetradecanol, while it has a larger interfacial concentration. The adsorption of SDS from aqueous solution is inferior energetically to that of tetradecanol from the hexane solution. It was also reported that dodecylammonium chloride and SDS differ appreciably in the values of the partial molar entropy and energy of adsorption while they have similar values in the partial molar volume change of adsorption under atmospheric pressure.

Lucassen-Reynders (30,31) studied single and mixed surfactant monolayers and also the interaction of mixed anionic/cationic surfactants thermodynamically. Góralczyk (32) calculated the changes of standard thermodynamic functions (ΔG° , ΔS° , and ΔH°) for anionic/cationic adsorption films. Rodakiewicz-Nowak (33) evaluated the bulk mixing ratios of cationic and anionic surfactants corresponding to their equimolar surface mixture both in the absence and the presence of inorganic salt. The surface mixing ratios of the components for three equimolar bulk mixtures in an excess of NaBr were also presented. Baret et al. (34,35) studied the kinetics of adsorption at an interface and presented theoretical models. A mixed model was proposed to include localized and mobile molecules in the adsorbed layer.

So far, mentioned researchers studied adsorption at liquid/air or liquid/liquid interfaces, while Shaeiwitz (36) measured adsorption rates of surfactants on solid surfaces in a packed bed apparatus. Using a nonequilibrium linear isotherm, adsorption and desorption coefficients were obtained and it was found that electrostatic repulsion or attraction played a minor role in the adsorption rate although the adsorptive capacity of a surfactant on a similarly charged surface as determined by equilibrium measurements was much less than for oppositely charged surfaces.

Rochester (37) obtained infrared spectrum to study adsorption on silica at the

solid/vapor and solid/liquid interfaces. Jednačak-Bišćan and Pravdić (38) investigated adsorption on the surface of controlled-pore glass using flow microcalorimetry. Adsorption isotherms were obtained and monolayer coverage and heats of adsorption were also estimated.

Morrison (39) worked on aqueous adsorption of anions onto oxides at pH levels above the point of zero charge. He found that certain anions continue to adsorb at pH significantly above those where positive surface site density falls to approximately zero. It was concluded that a mechanism for this involves hydrogen bonding of the residual hydroxy groups to the negatively charged surface oxide ions.

Patel (40) evaluated the surface entropy at the solid/liquid interface from adsorption isotherms on alumina and silica gel. Mukerjee and co-workers (41) studied the effects of unequal adsorption at vapor/liquid and solid/liquid interfaces.

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CHAPTER 2

INTERACTION OF IONIC SURFACTANTS AND DEWETTING TESTS

2.1. CATIONIC/ANIONIC SURFACTANT INTERACTION AT WATER/AIR AND WATER/FLUOROCARBON INTERFACE

These experiments illustrated the interactions of ionic surfactants at water/air and water/oil interfaces. Surface tensions and interfacial tensions were measured at water/air and water/fluorocarbon interfaces at room temperature using the blade method.

2.1.1. Chemicals

- 1) Cationic surfactant - Ammonyx Cetac, hexadecyltrimethyl ammonium chloride, 25% active from Onyx Chemical Company, Jersey City, NJ.
- 2) Anionic surfactant - Standapol ES-40, sodium myristyl ether sulfate, 60% active from Henkel Inc., Hoboken, NJ.
- 3) Freshly distilled water from potassium permanganate and sulfuric acid solution
- 4) Fluorocarbon oil - Genesolv D, trifluoro-trichloro-methane, from Allied Chemical Company

2.1.2. Measurements

- 1) The surfactants were dissolved in distilled water and then diluted to different concentrations separately.
- 2) Cationic and anionic surfactant solutions were mixed at different ratios. The chosen total concentrations were 5×10^{-5} and 5×10^{-6} mole/l (above and below critical micelle concentration of the 1:1 molar ratio).
- 3) Solution of 1:1 molar ratio surfactant solution was also diluted to different concentrations.

For all the solutions, the surface tensions were measured using a Rosano tensiometer (Arenberg Sage, Jamaica Plains, Mass.) with a sandblasted platinum blade except for cationic surfactant solutions where a mica blade was used. Next, equal volumes of Genesolv D and surfactant solutions were shaken in a separating funnel. The solutions were transferred into beakers until equilibrium was reached. Both surface and interfacial tensions were measured (teflon blade was used for interfacial tension measurements). The perimeter of the blades (platinum, mica, and teflon) were found by measuring known surface and interfacial tensions at different temperatures. Their dimensions were found as 5.34 cm, 3.45 cm and 5.21 cm respectively. All other unknown tension measurements were done at room temperature ($\sim 25^\circ\text{C}$). The dewettability of glass by the solutions was also tested visually by immersing the glass blade into the solutions.

2.1.3. Results

- 1) Surface and interfacial tensions of Standapol ES-40 solutions/Genesolv D systems were reported in Table 2.1. (See Figure 2.1).
- 2) Surface and interfacial tensions of Ammonyx Cetac solutions/Genesolv D systems were tabulated in Table 2.2. (See Figure 2.2). Dewettability of the aqueous solution on glass was also shown.
- 3) The surface and interfacial tensions of mixtures of Ammonyx Cetac and Standapol ES-40 solutions at different ratios with and without Genesolv D were measured. Concentrations of 5×10^{-6} and 5×10^{-5} mole/l were used. (See Table 2.3 and 2.4, Figures 2.3 and 2.4).
- 4) The surface and interfacial tensions of 1:1 molar ratio surfactant solution/Genesolv systems were reported in Table 2.5.
- 5) The aqueous Cetac solution was able to dewet glass and silicon but not alumina nor stainless steel when immersed and withdrawn from the Cetac solution.

2.1.4. Discussion

- 1) At room temperature, from Figure 2.1 and 2.2, the critical micelle concentrations of Standapol ES-40 and Ammonyx Cetac solutions are approximately 5×10^{-4} and 5×10^{-3} mole/l respectively.
- 2) From Figure 2.2, it can be seen that dewetting of glass by aqueous Cetac solution occurs within the range of 1×10^{-5} and 5×10^{-4} mole/l. Below 1×10^{-5} mole/l, insufficient long chain cations are adsorbed on the negatively charged glass surface to produce dewetting. Above 5×10^{-4} mole/l, a second layer of molecules is adsorbed on the hydrophobic chain of the first adsorbed layer (See Figure 2.5). This second adsorbed layer is wettable by water again.

Table 2.1 Surface and Interfacial Tensions of Standapol ES-40

Mole/l	γ	γ_D	γ_i
2×10^{-7}	69.00	70.00	40.20
2×10^{-6}	67.70	70.00	34.30
3×10^{-6}	64.96	70.00	32.20
5×10^{-5}	38.43	48.00	15.77
8×10^{-5}	35.20	43.65	5.00
5×10^{-4}	31.10	35.93	0.00 Foaming upon shaken
5×10^{-3}	36.90	39.50	0.00 w/o emulsion

γ = surface tension

γ_D = surface tension after shaking with Genesolv D

γ_i = interfacial tension

All in mN/m (dyne/cm)

Table 2.2 Surface and Interfacial Tension of Ammonyx Cetac

Mole/l	γ	Dewettability of Glass	γ_D	γ_i	
5×10^{-7}	71.00	W	71.00	39.24	
5×10^{-6}	70.57	W	71.00	27.33	
8×10^{-6}	68.00	ID	69.20	25.20	
5×10^{-5}	59.43	D	62.65	17.30	
5×10^{-4}	45.23	ID	46.15	0.00	Foaming upon shaken
5×10^{-3}	36.92	W	36.90	0.00	w/o emulsion
1.93×10^{-2}	36.92	W	36.90	0.00	w/o emulsion

W = wetted glass

D = dewetted glass

ID = incompletely dewetting

Table 2.3 Surface and Interfacial Tensions of Standapol and Cetac Solutions at Fixed Total Concentration of 5×10^{-6} mole/l

Mole % of Standapol	Mole % of Cetac	γ	γ_D	γ_i
0	100	70.57	71.04	27.33
20	80	44.86	52.46	14.60
40	60	37.39	50.00	11.00
50	50	33.65	49.68	8.78
60	40	39.26	52.93	8.78
70	30	46.73	58.96	10.00
80	20	50.47	65.46	11.70
90	10	58.42	69.18	25.38
100	0	64.96	70.04	32.20

Table 2.4 Surface and Interfacial Tensions of Standapol and Cetac Solutions at Fixed Total Concentration of 5×10^{-3} mole/l

Mole % of Standapol	Mole % of Cetac	Dewettility of glass	γ	γ_D	γ_i
0	100	D	59.43	62.65	17.30
20	80	D	30.83	40.21	3.00
40	60	D	27.92	35.53	0.00
50	50	D	25.03	27.12	0.00
60	40	ID	25.03	32.73	0.00
80	20	W	26.81	40.21	2.50
100	0	W	38.43	48.00	13.77

Table 2.5 Surface and Interfacial Tensions of 1:1 Ratio System

Mole/l	γ	Dewettability of glass	γ_D	γ_i
5×10^{-6}	30.65	W	49.68	8.78
2×10^{-5}	30.50	D	28.32	3.10
5×10^{-5}	25.03	D	27.12	0 o/w emulsion
5×10^{-4}	25.85	D	25.85	0 o/w emulsion
5×10^{-3}	27.85	D	25.85	0 o/w emulsion

Figure 2-1 Surface and interfacial tension of Standapol ES-40

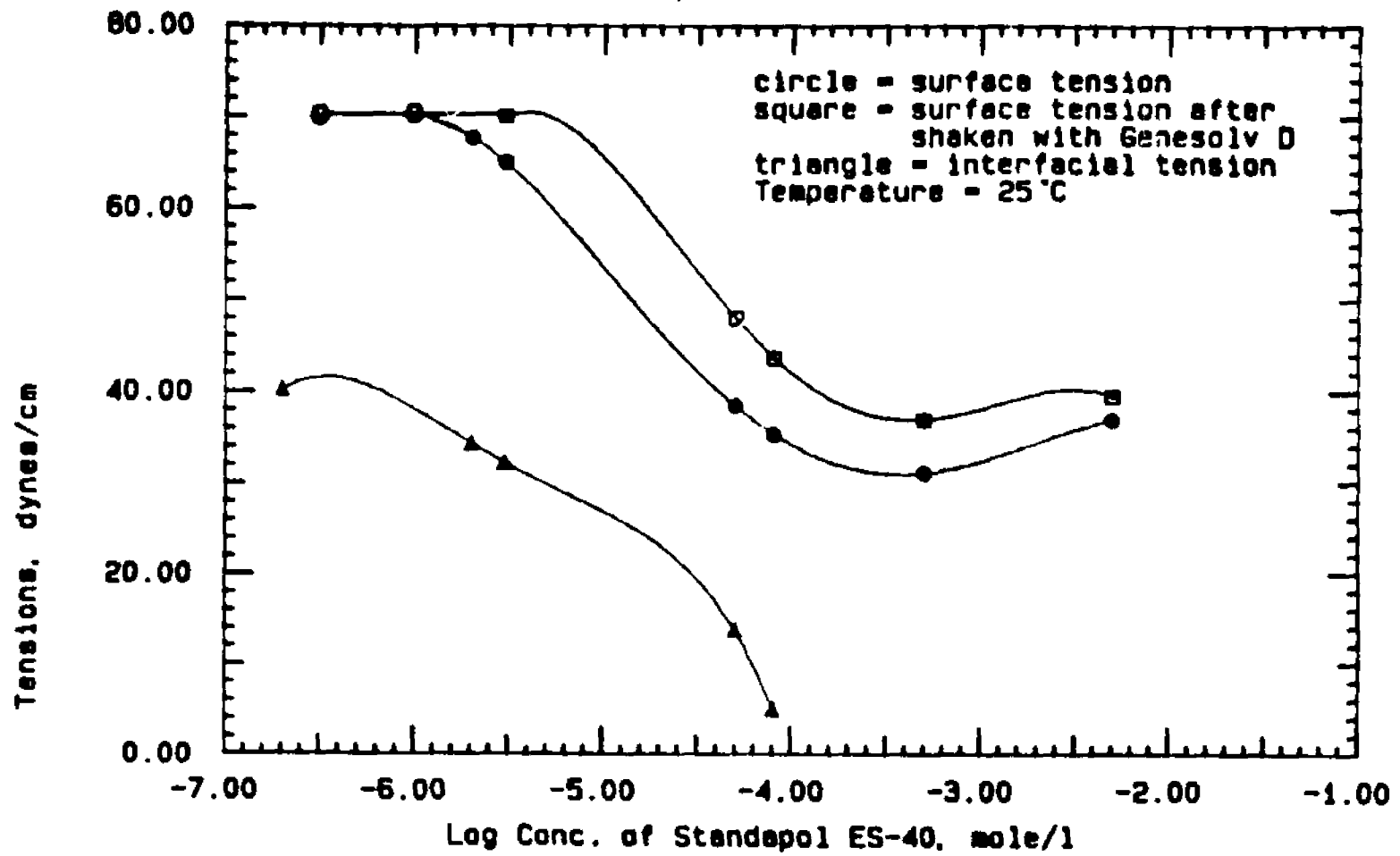


Figure 2.2 Surface and interfacial tension of Ammonyx Cetac

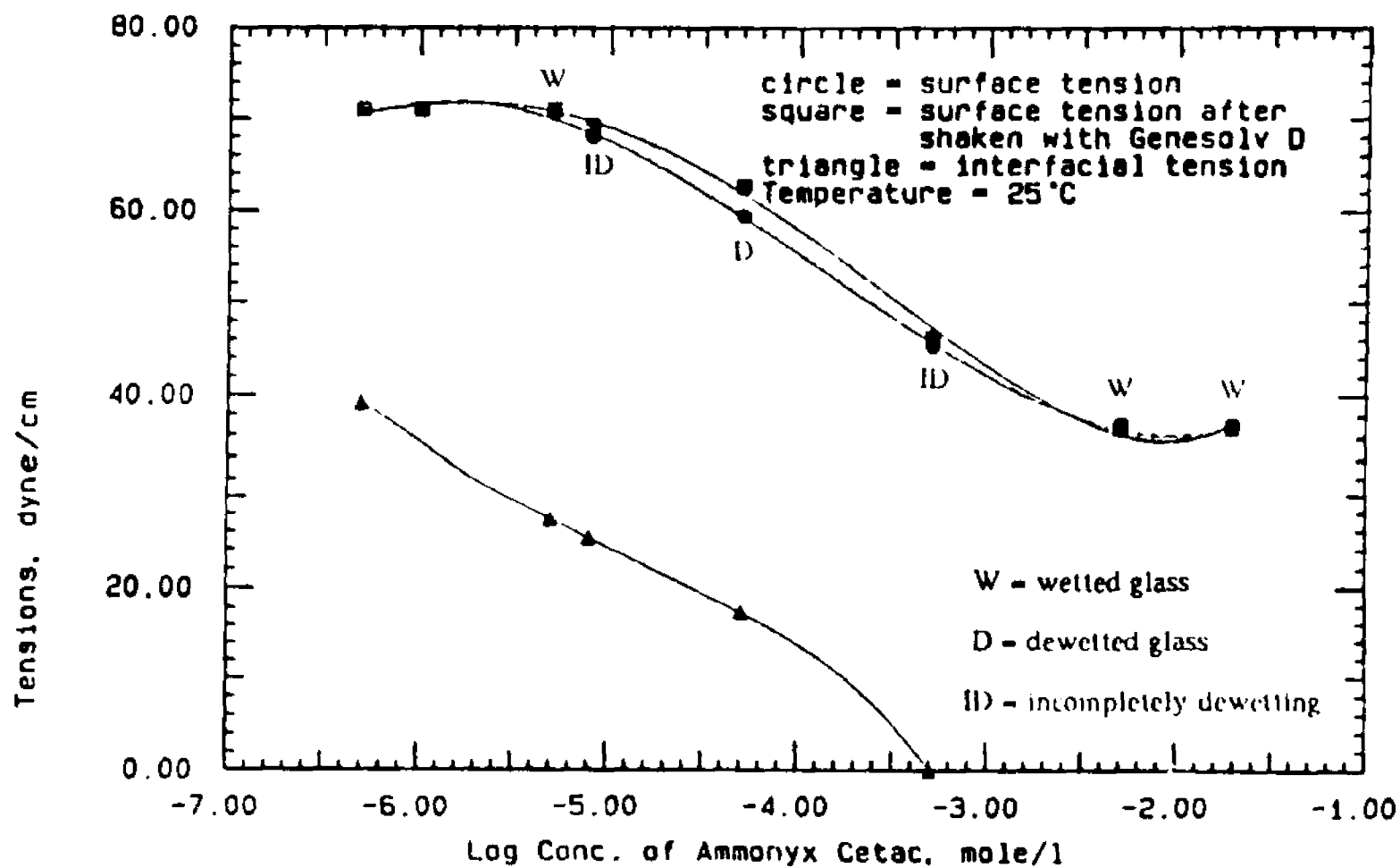


Figure 2.3 Surface and interfacial tension of Standapol ES-40 and Ammonyx Cetac mixtures at a total fixed concentration of 5×10^{-6} mole/l

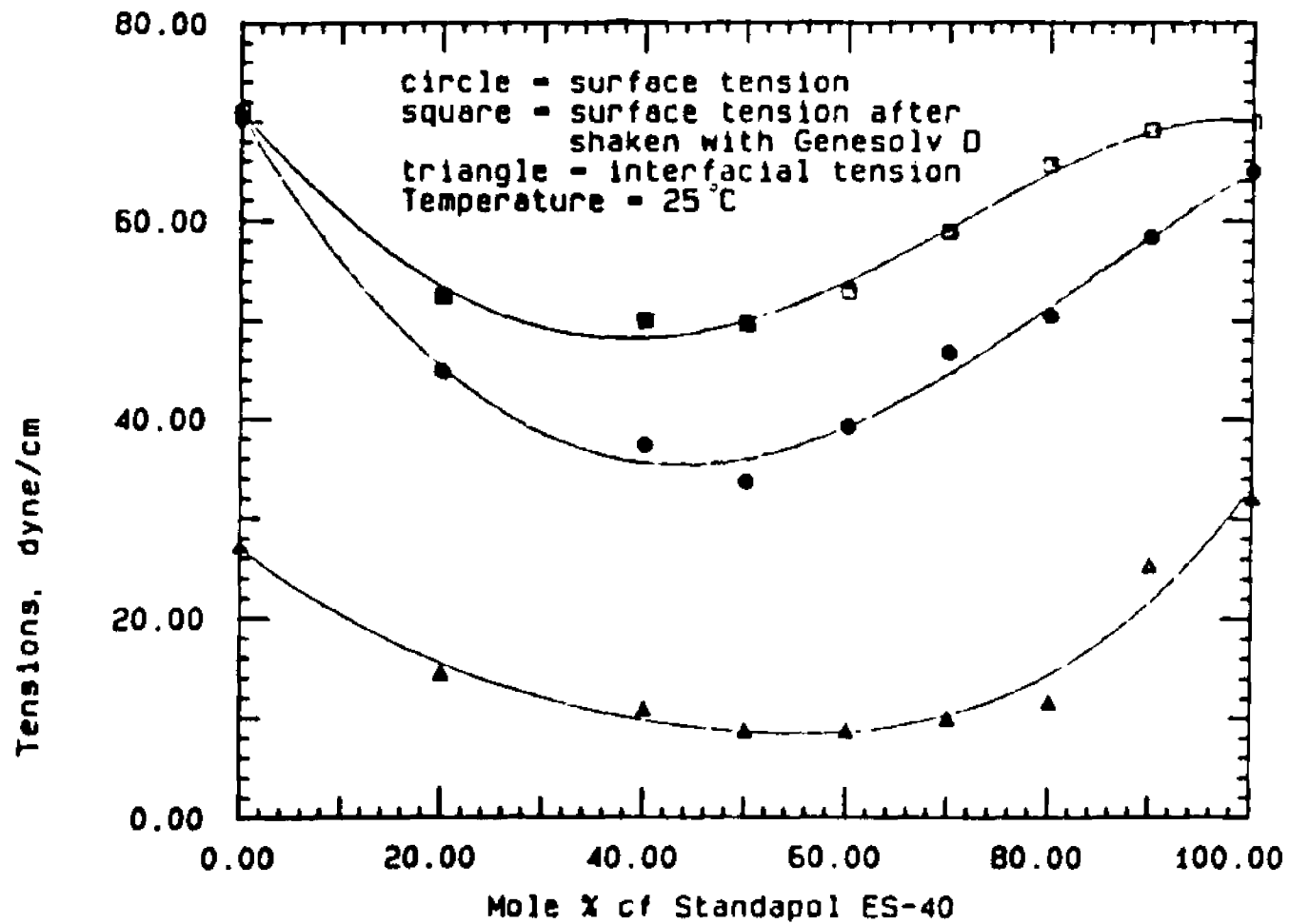
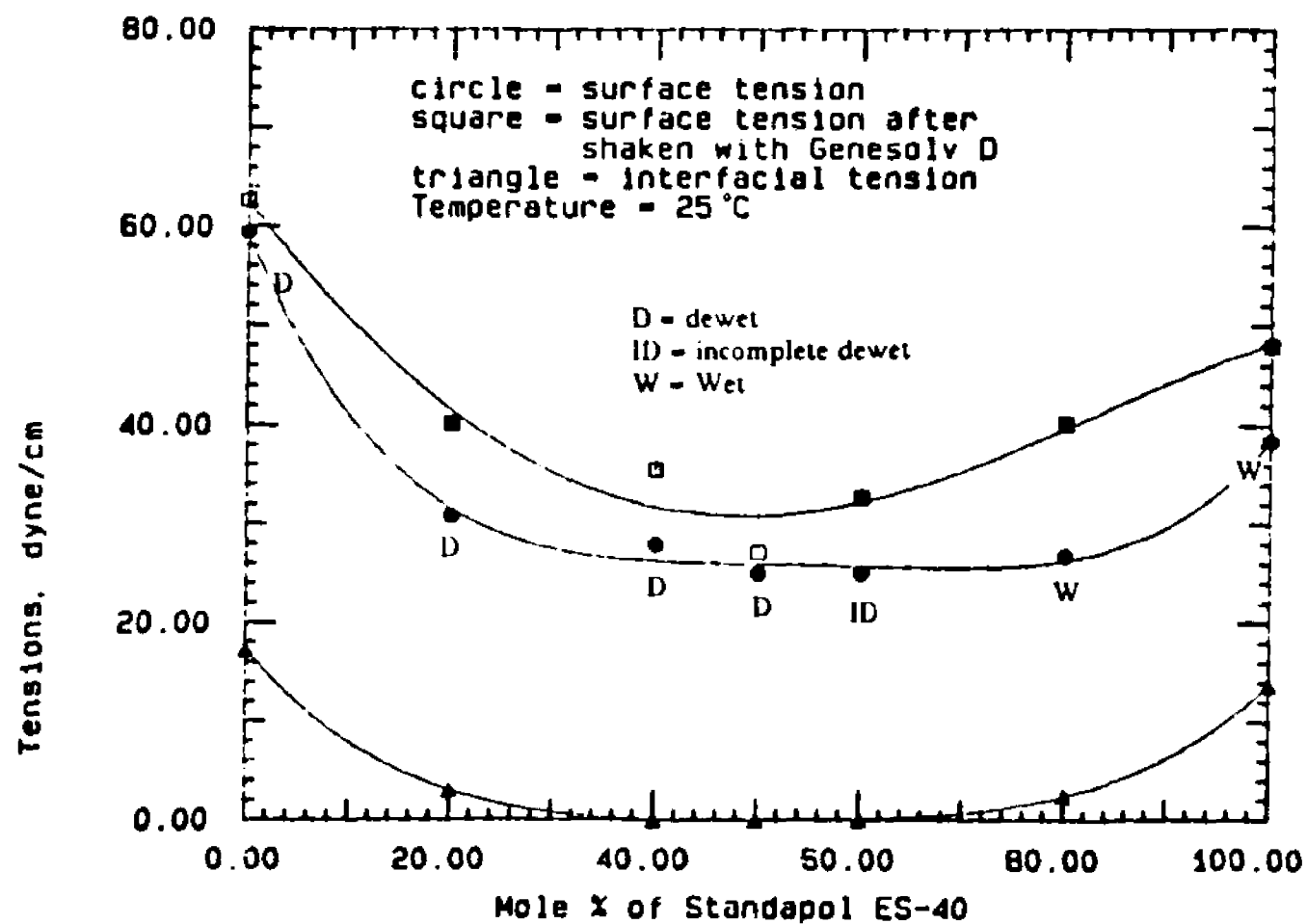


Figure 2.4 Surface and interfacial tension of Standapol ES-40 and Ammonyx Cetac mixtures at a total fixed concentration of 5×10^{-3} mole/l



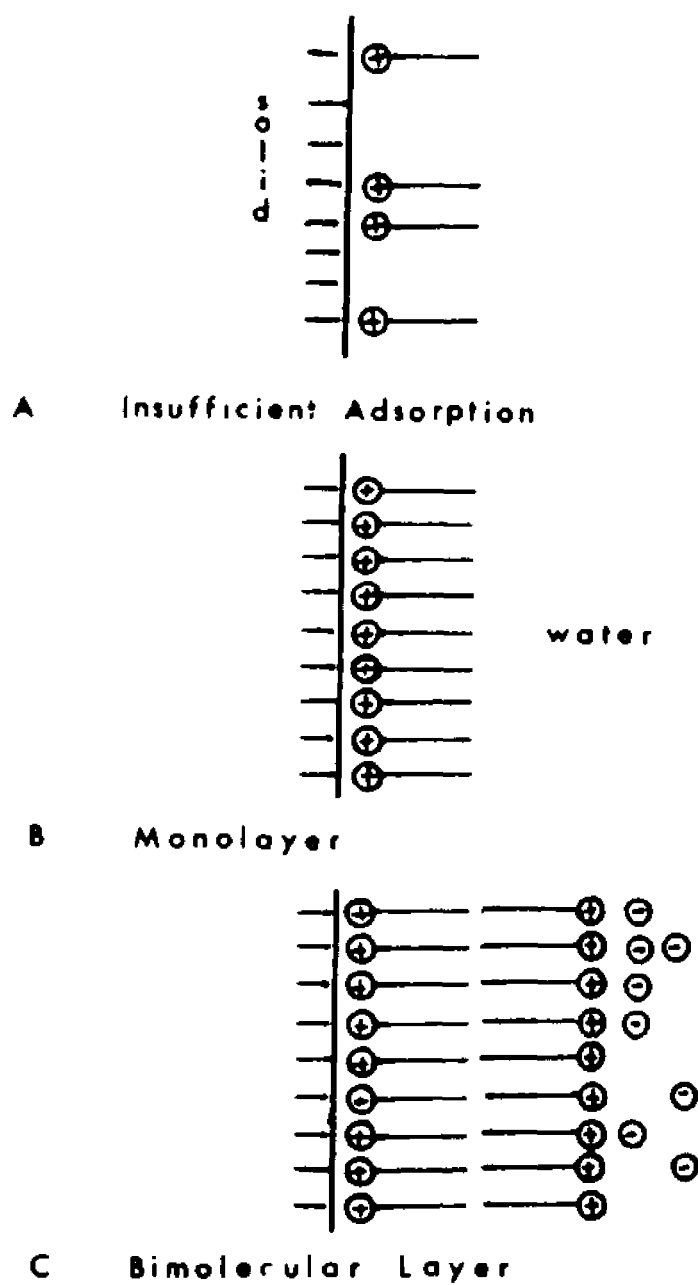


Figure 2.5 Adsorption of cationic surfactant at solid/water interface

Additional adsorption would indeed look like an adsorption on paraffin. In sense of contact angle, θ can be represented from equation (1.1) as :

$$\cos \theta = \frac{\gamma_s - \gamma_{w/s}}{\gamma_w} \quad (2.1)$$

The contact angle will increase from original zero as γ_s is reduced by adsorption of the surfactant. Observations (1-4) confirmed that long-chain cations from air/water surface are deposited onto a glass slide as it is withdrawn through the surface. It follows that there is more adsorption at the glass/air than at the glass/water interface. It is this monolayer adsorption that produces dewetting. However, at higher concentration of surfactant, a hydrophilic double layer reduces $\gamma_{w/s}$ to a very low value and θ decreases to give wetting again.

- 3) From both Figure 2.3 and 2.4 it can be seen that at the same total concentration, the minimum surface and interfacial tensions occur at 1:1 molar ratio. This shows that they form one to one association which is much more surface active than the individual surfactants. From Table 2.5, the critical micelle concentration of the 1:1 ratio solution is around 5×10^{-5} mole/l, lower than the individual surfactant solutions.
- 4) The decrease in interfacial tension before and after shaking the solution with Genesolv D is the largest when the ratio is 1:1. This shows that the 1:1 ratio is more soluble in Genesolv D than any of the individual surfactants.
- 5) The 1:1 molar ratio solution was able to dewet glass from 100% cetac solution up to 50/50 mixture solution.
- 6) It has to be reminded that dewetting by aqueous solution and by a fluorocarbon oil as the continuous phase are different. In the case of aqueous phase, hydrophilic solid surface becomes hydrophobic by adsorption of a monolayer of surfactant. Therefore, aqueous cetac (cationic) solution was only able to

dewet glass and silicon, highly negative charge surface but not the other two. Also, a second adsorbed layer is possible at high concentration as it is favored by the aqueous phase. However, dewetting by fluorocarbon requires only that $\gamma_{s/o}$ smaller than $\gamma_{w/s}$ provided that $\gamma_{w/o}$ is small and θ is close to 180° . A second layer adsorption is prevented by the oil continuous phase as water rises to the surface of the heavier oil and rewetting of the solid surface is not possible.

2.2. DEWETTING TESTS

Adsorption at solid/liquid interface was done by many researchers (4-8). Dewetting is one of the results of adsorption of the surfactant. In our study, dewetting tests were carried out using four different solid blades : glass, alumina, stainless steel and silicon. Drying solvents used were Dupont "Freon" T-DFC and Allied Chemical "Genesolv DRM". In Freon T-DFC, a combination of cationic and anionic surfactants were used while in Genesolv DRM, an amphoteric surfactant was used. In both solutions, the solvent was trifluoro-trichloro-ethane. All the solids were cleaned with a fresh sulfochromic acid solution and then with distilled water. Finally, the solids were dipped into water at different pH (HCl/NaOH mixture). The wetted solids were first immersed into one of the solvents. Then, they were taken out and visually examined to see if dewetting took place. The number of immersions required to dewet the solid were noted. (See Table 2.6).

Results indicate that dewetting could be spontaneous or required several immersions. It was then assumed that the rate of adsorption of the surfactant onto the solid surface can vary greatly. Overall, Dupont "Freon" T-DFC worked better than Allied Chemical "Genesolv DRM" as a dewetting agent, as more immersions were necessary for "Genesolv DRM" to dewet the same solid. In the case of glass, as soon as the edge of the glass touched the Dupont "Freon" T-DFC liquid surface, a capillary explosion was observed. No complete immersion was necessary and dewetting was spontaneous. Although Genesolv DRM was able to dewet the solids, traces of water still could be observed on the solid surface. It did not dewet as thoroughly as Freon T-DFC. The pH of the water did not seem to affect the dewetting performance of the solutions except at high or low pHs.

In our study, glass, stainless steel, and silicon surfaces have a negative zeta potential while alumina is slightly positive when immersed in water.

Table 2.6 Dewetting Test

pH	Glass		Alumina		Stainless Steel		Silicon	
	Dupont	GRM	Dupont	GRM	Dupont	GRM	Dupont	GRM
1.4	D1	D2	D3	D8	D4	D4	D2	D2
2.1	D1	D2	D2	D5	D4	D4	D2	D2
3.0	D1	D2	D2	D5	D4	D4	D2	D2
3.8	D1	D2	D2	D6	D4	D4	D2	D2
4.3	D1	D2	D2	D6	D4	D4	D2	D2
5.15	D1	D2	D2	D6	D4	D4	D2	D2
6.2	D1	D2	D2	D5	D4	D4	D2	D2
7.1	D1	D2	D2	D5	D4	D4	D2	D2
8.8	D1	D4	D2	D6	D4	D4	D2	D2
10.5	D1	D4	D3	D5	D5	D5	D2	D2
11.4	ID3	W8	D6	D5	D7	D5	D3	W15

D = dewet

ID = incomplete dewet

W = Wet

1 = instant dewetting

2 = 1 immersion

3 = 2 immersions

4 = 3 immersions

2.3. CONCLUSION

It was shown that aqueous cationic solution can dewet glass and silicon even though rewetting occurs again at higher concentration. Also, cationic and anionic surfactants form 1:1 molar ratio association which is more surface active and more soluble in fluorocarbon oil than the individuals and at other ratios. Solubility of surfactant in the fluorocarbon oil is important as the concentration of surfactant in the fluorocarbon phase will decrease if the surfactant is extracted by water, an undesired phenomenon. The cationic/anionic complex is almost completely insoluble in water while the amphoteric surfactant could form an aqueous micelle solution. Chain length of the amphoteric surfactant has to be long in order to prevent solubilization in water. Therefore, it is an advantage to use a cationic/anionic combination so that the surfactants would solubilize in the fluorocarbon oil without being extracted in the water phase.

It seems that solid/surfactant interaction depends mainly on nature and the structure of the surfactant, dielectric constant of the solvent, chemical and the physical structure of the solid. When anions and cations are in the fluorocarbon solvent, they interact sufficiently to prevent water solubilization but the interaction is weak enough to allow adsorption on the immersed solid surface. It is logical that the cationic/anionic complex will split upon immersion of a charged solid and the opposite charged surfactant will adsorb onto the solid which is responsible to the dewetting.

From dewetting tests, it was evident that electrostatic forces play an important role in the adsorption of the surfactants. It is well known that glass surface is highly negative while alumina is slightly positive. Opposite charged surfactant will adsorb at the solid surface producing a hydrophobic surface. That explains the fact that the cationic/anionic combination in Freon of Dupont dewets better than the amphoteric surfactant alone in Genesolv of Allied Chemical. The

cationic surfactant will dewet negative charged surfaces while the anionic will dewet positive ones. By the same token, the amphoteric surfactant will also be adsorbed in a similiar manner. However, as the same sign of charge remains in the surfactant, i.e. there is no splitting of the surfactant, there is bound to be repulsion between the solid surface and the molecule. This weakens the adsorption and it did not perform as well as the cationic/anionic combination. That is also the reason why the cationic surfactant was able to produce spontaneous dewetting, but the amphoteric one did not.

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CHAPTER 3

ELECTROCAPILLARITY

3.1. APPLICATION OF ELECTROCAPILLARITY TO OUR STUDY

The point of zero charge (PZC) or the isoelectric point of different solids has been studied by many authors (1-4). The PZC of glass was found to be between pH 2.3 to 3.7 (5-7). For alpha-alumina, it was at a pH 9.1 (2,3). The solid surface will be positively charged at a pH lower than PZC and negatively charged above it. It can be seen that different solids have various surface charges and electrostatic forces may play a major role in determining adsorption at the solid/liquid interface. As shown in section 2.2, dewetting tests indicate clearly that surfactant/solid surface interaction varies widely. In addition, these interactions probably depend on:

- 1) the nature and surface charge of the solid
- 2) the molecular structure and charge of the surfactant

It was decided to use the electrocapillary method to study the adsorption of various cationic, anionic and amphoteric surfactants at a water/mercury interface at different surface charge. The choice of this method may be justified for several reasons :

- 1) The mercury/water interface is a totally polarizable interface.
- 2) The interface is constantly regenerated (clean and reproducible)
- 3) The sign and value of the interfacial electrical charge can be varied.
- 4) The interfacial tension and electrical capacitance can be determined.

The structure of solids is different from one to the another. However, using mercury, of which the surface charge can be varied, adsorption due to electrostatic forces can be justified using different surfactants. This serves as a model surface

to study the adsorption of different types of surfactants on different surface charged solids.

3.2. ELECTROCAPILLARY CURVE

3.2.1. General Review

The first determinations of the relationship between surface tension and polarizing potential of the mercury/water interface were due to Lippmann (8-11). Mercury was used because it is assumed to be completely polarizable. No ions discharge from the solution at the interface. The potential difference between the two phases can be altered with wide limits by applying an external potential difference.

According to Lippmann, in a very narrow capillary, an interface between mercury and an aqueous solution is kept at a chosen position by applying a suitable hydrostatic pressure when a given polarizing tension, V , has been set up between mercury electrode and the calomel electrode. A typical curve between the interfacial tension, γ_i and the polarizing potential is shown in Figure 3.1. This roughly parabolic curve is known as the *electrocapillary curve*. Lippmann derived the following equation for the interface :

$$\left. \frac{\partial \gamma_i}{\partial V} \right|_{T, P, \text{all } \mu_s} = - \left. \frac{\partial Q}{\partial A} \right|_{T, P, \text{all } \mu_s} = - \sigma \quad (3.1)$$

where T = temperature

P = pressure

Q = charge on the mercury

A = area of the interface

μ = chemical potentials

σ = surface charge per unit area

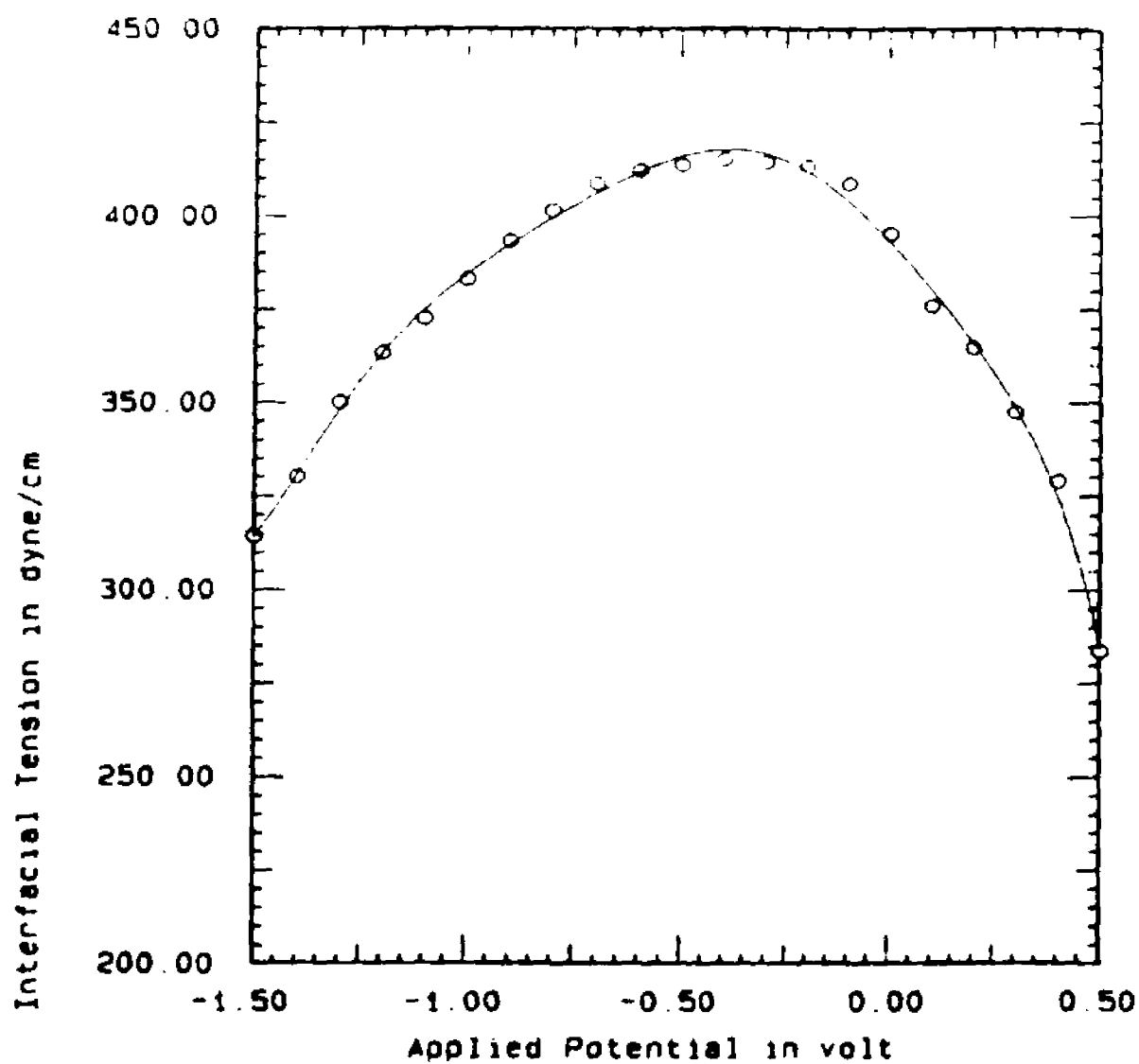


Figure 3.1 Typical electrocapillary curve, 0.01N Potassium Nitrate

The electrocapillary maximum is known as the point of zero charge (PZC). This does not necessarily represent no charge at all. It probably is an indication that the overall charge on the mercury, σ is zero or $\frac{\partial \gamma_i}{\partial V} = 0$ at that point. On the rising or the anodic branch, the mercury bears a positive charge and the lowering of the interfacial tension is due to the adsorption of the anions from the electrolyte solution. In the case of the descending or cathodic branch, cations are adsorbed on the negatively charged mercury. The first differential $\frac{\partial \gamma_i}{\partial V}$ gives the charge of the mercury surface. The second differential $\frac{\partial^2 \gamma_i}{\partial V^2}$ gives the differential capacity of the double layer. If the capacity of the double layer is a constant, the electrocapillary curve would be exactly parabolic. Therefore, the width of the parabola gives the mean value of the capacity and the deviation from a parabolic shape reflect the non-constancy of the capacity of the double layer. The absolute height of the electrocapillary curve is relatively unimportant for double layer considerations. Actually, the interfacial tension can be calculated from the drop time if the diameter of the capillary and the hydrostatic height are known. The conversion of drop time into interfacial tension will be discussed later in section 3.4.

Grahame (12-14) defined the term "capacity" as integral (or static) and differential capacity. Integral capacity is represented as an ordinary condenser by the equation :

$$K = - \frac{\sigma}{E} \quad (3.2)$$

where K = integral capacity

σ = specific charge on the surface of the solid in coulombs/cm²

E = potential difference between solid and solution reckoned
as if it is zero at the potential of the maximum of the
electrocapillary curve

Regarding the accumulation or depletion of electrons at the surface of the solid immersed in a liquid as an ideal case of surface adsorption (adsorbed particles are electrons), equation (3.2) was obtained by Grahame. Using Gibbs adsorption equation it was converted into electric units as :

$$\frac{d \gamma_i}{d E} = - \sigma = K E \quad (3.3)$$

Since $\frac{d \gamma_i}{d E}$ is zero at the electrocapillary maximum, and K can never be zero, it follows that E must be zero at electrocapillary maximum. Differentiated equation (3.2) once more, it becomes :

$$\frac{d^2 \gamma_i}{d E^2} = - \frac{d \sigma}{d E} = \frac{d}{d E} \left[K E \right] = C \quad (3.4)$$

This equation defines C , the differential capacity and shows clearly the distinction between the integral and differential capacity. Thus K is related to the total potential difference whereas C is the rate of change surface charge with respect to the potential. The relationship between the two is :

$$C = K + E \left[\frac{d K}{d E} \right]_{\mu} \quad (3.5)$$

or

$$K = \frac{1}{E} \int_0^E C \, d E \quad (3.6)$$

The above equations give a means of calculating the capacity from the other.

3.2.2. Literature Review

Frumkin (15) developed a model for adsorption at the unpolarized surface and it is given by :

$$\frac{\Theta}{1-\Theta} = B_0 a e^{2\alpha\Theta} \quad \left[V = 0 \right] \quad (3.7)$$

in which Θ = fractional surface coverage

a = solute activity

B_0 and α = constants

Then, Frumkin also showed that adsorption at the polarized surface can be a model for a double layer of two condensers in parallel, one containing only water, the other only adsorbate, so that :

$$Q = Q_w (1 - \Theta) + \Theta C' (V - V_N) \quad (3.8)$$

Then, it leads to :

$$\frac{\Theta}{1-\Theta} = B_0 a e^{2\alpha\Theta} e^{\left[\frac{S\phi}{RT} \right]} \quad (3.9)$$

where S is the molar area of adsorbate ($\Theta = 1$) and

$$\phi = \int_0^V \left[Q_w - C' (V - V_N) \right] dV \quad (3.10)$$

with Q_w = interfacial charge density at polarization V relative to the electrocapillary maximum

C' = capacitance per unit area of the adsorbate condenser
(assume independence of polarization)

V_N = shift in potential of the electrocapillary maximum as Θ changes from 0 to 1

V = polarization potential referred to the electrocapillary maximum in absence of adsorbate

Hansen and co-authors (16-23) pursued this model further and showed that the dependence of differential capacitance on polarization and adsorbate activity is :

$$\theta_{app} = \frac{C_\infty - C}{C_\infty - C'} \quad (3.11a)$$

or

$$\theta_{app} = \theta \left[1 - \frac{S}{R T} \left| \frac{1 - \theta}{1 - 2 \alpha \theta} \right| \left| \frac{[Q_\infty - C' (V - V_N)]^2}{[C_\infty - C']} \right| \right] \quad (3.11b)$$

where C_∞ and C are the differential capacitances per unit area in absence and in presence of adsorbate. Isotherms of organic compounds from aqueous solution were prepared using the above equations.

Parsons and co-workers (24-26) modified the Langmuir's isotherm for different particle size of solute and solvent. Two limiting forms of adsorption isotherm were considered based on Langmuir's isotherm and on a two-dimensional hard sphere equation of state. The electrical charge was taken as the primary electrical variable. Hills and Paynes (27-29) studied the temperature and pressure dependence of the double layer capacity at the mercury/liquid interface. The surface excess entropy and volume were computed by the thermodynamic method and interpreted in terms of the adsorbed solvent's layer in the inner region of the double layer. It was then extended to the systems in which the anions are specifically adsorbed. Conway et.al. (30-36) studied adsorbed phases at electrode interfaces in relation to solvent displacement and the Langmuir and Flory-Huggins types of adsorption isotherms. He suggested that for adsorption of molecules for which the size factor is greater than one, failure to include a size factor term in the isotherm leads to errors in the evaluation of any interaction effects in the adsorption behavior. The Esin and Markov effect was also discussed in two principle surface dipole terms as :

- 1) due to displacement of oriented solvent molecules

2) due to orientation of the organic adsorbate itself.

Both are dependent on surface charge.

Wroblowa and Müller (37) suggested single imaging in the metal plane rather than multiple imaging and confined the region of low dielectric constant to a monolayer of adsorbed water. Levine (38) developed a statistical mechanical theory of the dielectric properties of the Stern inner region at the mercury/water interface in the absence of the specific adsorption of ions. His model of the region is a plane monolayer of polarizable water (point) dipoles at fixed surface density. This layer is sandwiched *in vacuo* between two continuous media, the aqueous phase and the mercury phase which carries a surface charge. Dipole-dipole interactions and dipole imaging due to the two continuous media are also considered.

Chin and Genshaw (39) determined the anion adsorption on platinum using an optical technique, ellipsometry. They found that the order of increasing in adsorption to be : SO_4^{2-} , Cl^- , Br^- , I^- , and the adsorption of ClO_4^- and F^- are less than the limit of detection ($\theta = 0.01$). Tilak and Devanathan (40) investigated the adsorption of nitrate and phthalate ions at the mercury/solution interface. It was recommended that the hydration structure of the adsorbed ion has to be considered in any examination of the fine structure of the electrical double layer. Payne (41) measured double-layer for a mercury electrode in amide solvents. He concluded that the capacity generally decreases with increasing molecular weight of the amide solvents but is not directly dependent on the macroscopic dielectric constant. Barradas and Hermann (42) studied temperature effect on lithium chloride solutions by electrocapillary. The significance of a certain peculiar charged effect was explained in terms of ion-water interactions and the importance of the role of adsorbed water in the double layer was emphasized. Doblhofer and Mohilner (43) investigated the electro-adsorption of 5-chloro-1-pentanol at mercury/solution

interface. It was concluded that the electro-adsorption isotherm is neither congruent with respect to the electrode potential nor with respect to the charge density. It was also proved that the well known necessary condition for congruence electro-adsorption with respect to electrode potential or charge density is a sufficient condition.

Holmqvist (44) used oscillographic polarography to study adsorption of surfactants. Matsuda and Tamamushi (45) determined some of the electrochemical kinetic parameters during the growth of the dropping mercury electrode. It was found that the relationship between the rate constant of Cd(II) and coverage of the uncharged surfactant was not linear and follows the equation based upon Parsons' model of the blocking effect. Guidelli and Moncelli (46) studied the influence of diffusion control adsorption of surfactant at the mercury/solution interface. As the bulk concentration of surfactant is gradually increased, the interfacial tension shows an abrupt drop from a non-equilibrium value equal to that in absence of the surfactant to equilibrium values corresponding to full coverage. Based on the diffusion-layer concept under the assumption that the surfactant is adsorbed according to the Frumkin isotherm in the absence of diffusion equilibrium, a method was proposed for determining the adsorption coefficient and the attraction factor of surfactant from interfacial tension versus $\log C$ (bulk surfactant concentration) curves.

Cosović (47) investigated the adsorption of mixtures of surfactants on the basis of capacity current measurements using the polarographic method of discontinuously changing the potential known as the Kalousek commutator technique. Vollhardt and Modrow (48) examined different models for the adsorption process of surfactants by non-linear regressions analysis. The frequency dependence of electrode admittance of sodium decyl sulphate solutions above the critical micellar concentration was measured at the more negative adsorption/desorption potential.

Diffusion control, adsorption control and combinations in parallel processes could be selected as the model by non-linear regression. Müller and Dörfler (49) studied the relationship between electroadsorption and the inhibition behavior of homologous phosphine oxides using d.c. polarography. The comparison of the rate constants of the electrode transfer reaction of Cd^{2+} with the surface pressure values shows the rate constants decrease linearly with increasing surface pressure values. It is also shown that the inhibitory effect grows as the length of the alkyl groups increases. Kaisheva, Kaishev and Matsumoto (50) measured the differential capacity of a stationary mercury electrode as a function of electrode potential and concentration of dodecylhexaoxyethylene glycol monoether by the impedance bridge method. A spline regression model was used to predict the differential capacity for any potential and surfactant concentration in the interval studied. The free energy of adsorption and some other parameters characterizing the adsorption of the surfactant was determined.

Watanabe, Matsumoto, Tamai and Goth (51) investigated the electrocapillary phenomena at oil/water interfaces with potassium chloride in the aqueous phase and surfactant in the oil phase. It was found that the interfacial tension was suppressed over the cathodic or the anodic polarization range depending on whether the surfactant used was cationic or anionic. Using the Lippmann-Helmholtz equation, the water side was found to be charged as a result of the counter ion layer formed corresponding to the adsorption of ionic surfactant on the oil side. An amphoteric material, lecithin, was also studied (52). It was found that lecithin dissolved in the oil phase behaved as the cationic and anionic, depending on the pH of the aqueous phase. This showed that the ionic groups of lecithin penetrate into the aqueous side of the interface. Watanabe and Tamai (53) also studied tetrabutylammonium chloride in methylisobutylketone (the oil phase) and surfactant in the aqueous phase in addition to the inorganic electrolyte.

Linear relations were found between the interfacial excess of the surfactant and the cubic root of its concentration, as well as of ionic strength of the aqueous phase.

So far, most researchers have done experiments on mercury/water or oil/water systems only. Mercury/oil studies have rarely been done. The experimental set up is described in the next section for mercury/water. However, it is not limited to the study of adsorption at mercury/water interface only. Non-aqueous solution can be used instead of water upon using a suitable reference electrode.

3.3. APPARATUS AND PROCEDURES

The mercury used was cleaned in a setup as shown in Figure 3.2. It was filled with 30% nitric acid solution up to the level that it almost came out from the bottom outlet. Mercury was poured into the funnel. A sharp needle was used to make a tiny hole in the filter paper. Mercury was filtrated through this pin-hole to get rid of the large impurities. Mercury was then washed while it passed through the nitric acid solution and then came out from the bottom outlet along with some acid. It was collected in a clean breaker. After all the mercury had run through the acid, the side outlet was opened so that some of the acid was drained. Deionized and then distilled water was added to the column and to the breaker to dilute the remaining acid. Most of the acid solution was drained. The remaining mercury and acid in the column and in the breaker were put into a separating funnel. This cleaned mercury was used for the electrocapillary experiment.

The experimental setup was similar to Lippmann's as shown in Figure 3.3. The platinum electrode was the counter electrode. Saturated potassium chloride calomel electrode and the mercury electrode were the reference electrode and

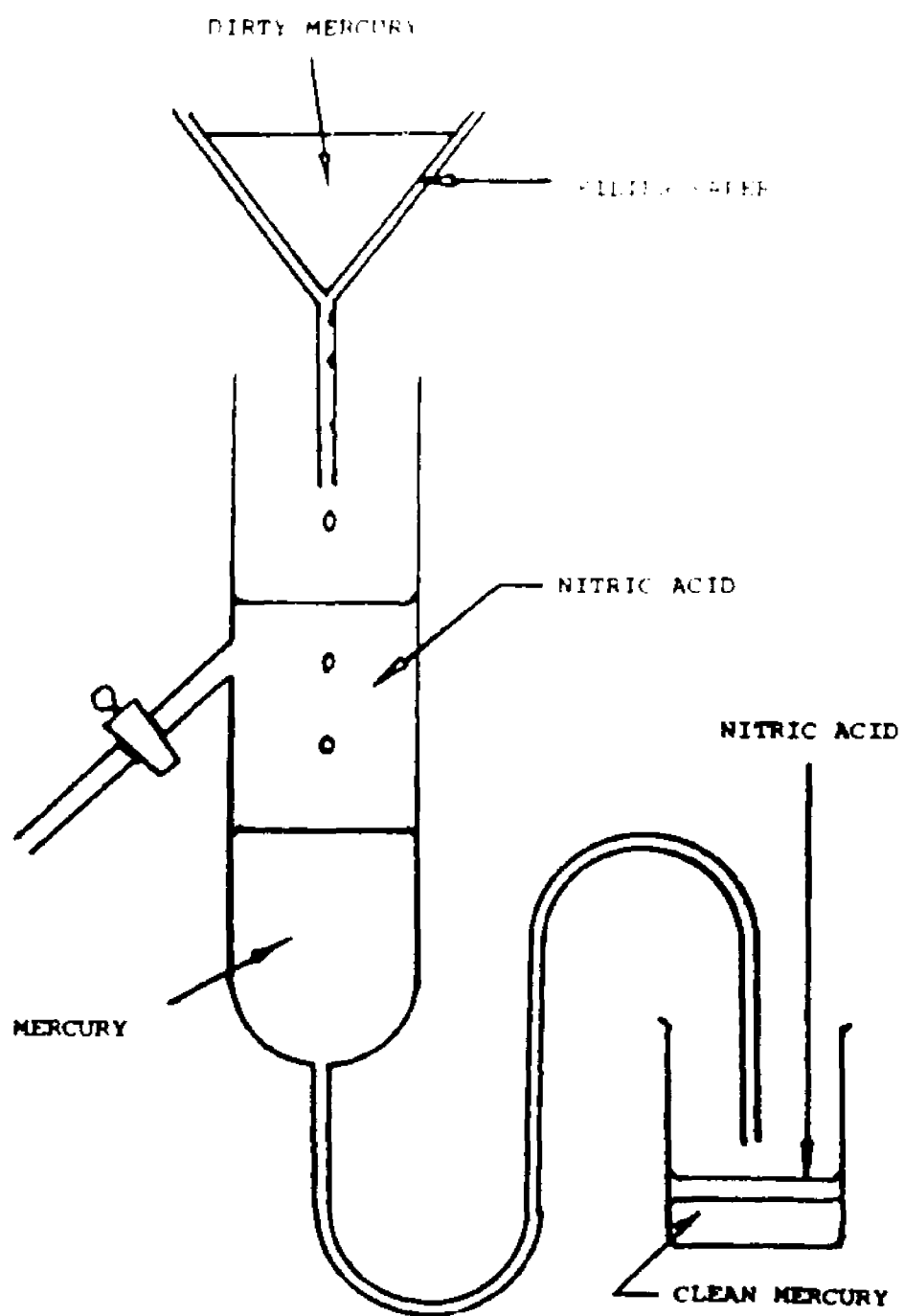


Figure 3.2 Apparatus to clean mercury

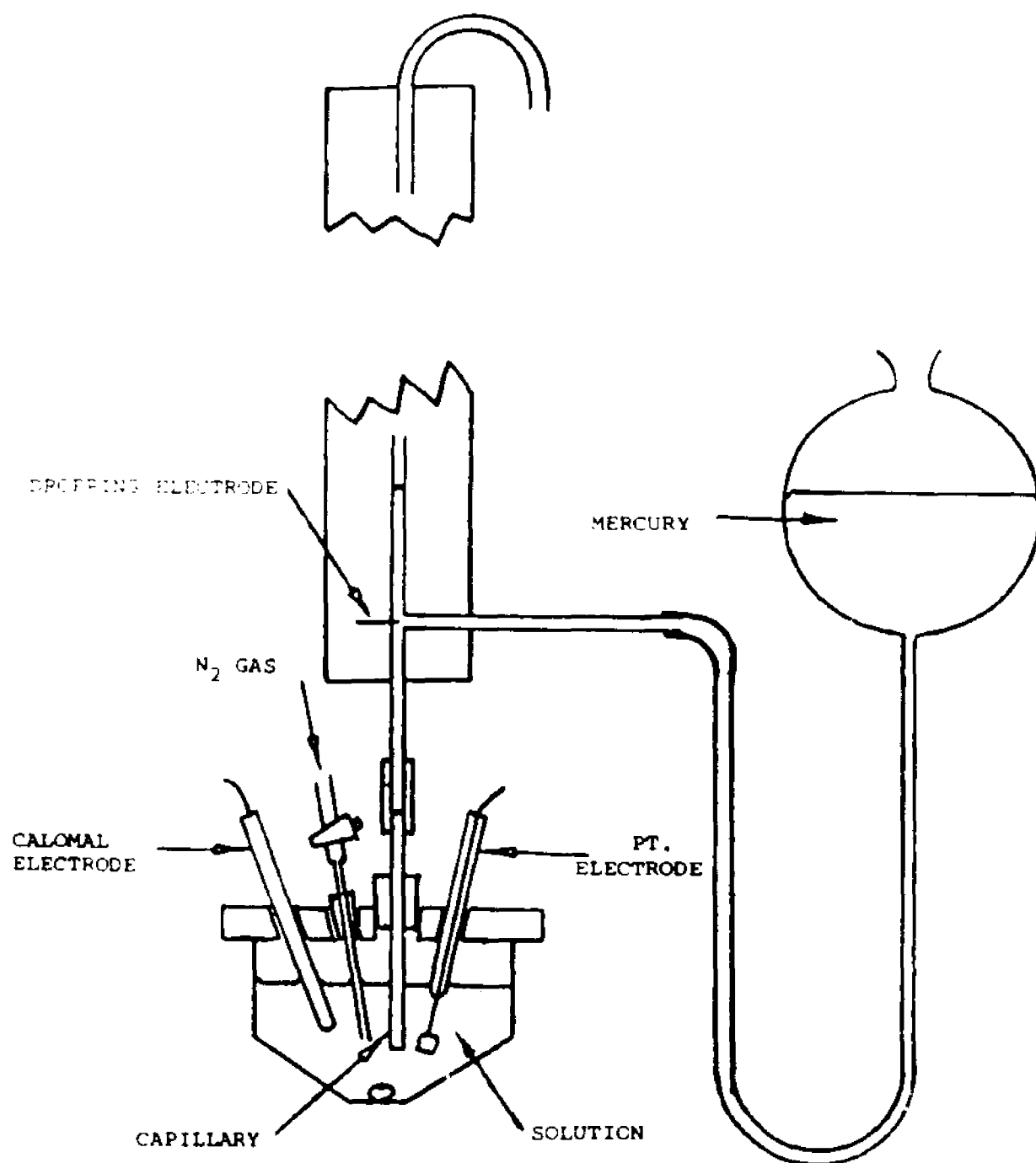


Figure 3.3 Apparatus for electrocapillary experiment

dropping electrode respectively. All three electrodes were fed into the cyclic voltammograph (Model CV-27, Bioanalytical Systems Inc., West Lafayette, IN 47690) in the cell mode. The electric potential could be adjusted and the voltage across the mercury and the solution was measured by the Voltammograph. The current was fed as an output to the Y-axis of a recorder (Model 815, X-Y Plotamatic Recorder, MFE Corp., New Hampshire 03079). A self-contained time-base generator (Model 7T, MFE Corp., N.H. 03079) was connected to the X-axis as an input of the recorder to control the sweep speed.

Cleaned mercury was poured into the reservoir and a desired hydrostatic height was kept constant in the column. As the mercury was dropping out from the capillary, the cup containing the solution was put on. This was to assure that no solution went inside the capillary which might be plugged easily. This also prevents adsorption of surfactant onto the inside wall of the capillary. If surfactant solution enters the capillary, due to a strong adsorption of surfactant, the contact angle will be changed and drop time will be affected.

Nitrogen gas (Union Carbide Corp., Linde Div., N.Y.) was passed through a catalysis Radox (Fisher Chem., Fairlawn, N.J.) to get rid of any possible oxygen from the tank and it was bubbled through distilled water. This fresh, pure nitrogen was used to bubble in the solution in the cup to eliminate any oxygen. After bubbling for fifteen minutes, nitrogen gas was turned off. Mercury was allowed to drop at an applied potential ranging from 0.00V to -1.50V. Beyond this range, mercury will not be completely polarized. The current was measured continuously. The limiting faradic current flow at the dropping mercury electrode (DME) under usual polarographic conditions (i.e. within the limits of polarization), increases monotonically during the life of the drop and it can be described approximately by the Ilkovic equation :

$$i_d = 708 \pi D_0^{\frac{1}{2}} C_0^* m^{\frac{2}{3}} t^{\frac{1}{6}} \quad (3.12)$$

where i_d = faradic current in ampere

n = electrical charge of the ion

D_0 = diffusion coefficient in cm^2/sec

C_0^* = concentration in the bulk in mole/cc

m = mass flow rate of mercury in mg/sec

t = drop time measured from the birth of the drop in second

When the drop fell off from the capillary tip, the current dropped back to zero. From this discontinuity of the current, drop time can be determined.

3.4. RELATIONSHIP BETWEEN INTERFACIAL TENSION AND DROP TIME

Interfacial tension is an important parameter for studying an interface. Other interfacial variables, e.g. adsorption isotherms, in case of electrocapillary, interfacial charge, and differential capacity of the Hg/solution interface can all be determined from interfacial tension measurement. However, direct measurement of interfacial tension requires special and precise apparatus and the experiment is time consuming. A simply method is to measure the drop time of the mercury using a time calibrated recorder and then to calculate the interfacial tension from the drop time since it is proportional to interfacial tension.

The basic relationship between the interfacial tension and drop time of a dropping mercury electrode (d.m.e.) has been summarized by Corbusier and Gierst (54, 55). However, their final equations contain numerical coefficients which are not valid for capillaries having different parameters. The derivation of Sathy-anarayana (56) is usable. Nevertheless, with the aid of a digital computer, more terms can be considered for higher accuracy of conversion of drop time into interfacial tension within a short computing time.

The mass of a mercury drop surrounded by a solution at the instant of detachment from the tip of the capillary is given by :

$$\alpha M_d g = 2 \pi R \gamma_i \quad (3.13)$$

where α = buoyancy factor = $\frac{\rho_{Hg} - \rho}{\rho_{Hg}}$

ρ_{Hg} = density of mercury (g/cc)

ρ = density of the solution

M_d = mass of mercury drop in air at the instant of detachment

g = acceleration due to gravity (cm/sec²)

R = internal radius of the capillary (cm)

γ_i = interfacial tension (dynes/cm)

However, the mass M_d of the drop is subjected to two corrections :

- 1) Harkins' correction due to incomplete detachment of the mercury drop from the tip of the capillary
- 2) Kucera's correction due to the back pressure exercised by the interfacial tension γ_i .

For the first correction, one can write :

$$M_d = m t (1 + \beta) \quad (3.14)$$

where mt = the mass (g) of the detached drop in air

m = mass flow rate of mercury in the solution (g/sec)

t = drop time of mercury (sec)

β = Harkins' correction term

Using Harkins' data (57), Smith (58) approximate β as :

$$\beta = 3.680 R (m t)^{\frac{1}{3}}$$

or using equation (3.13), it becomes :

$$\beta = 3.680 \gamma \left[\frac{\alpha g}{2 \pi R \gamma_i} \right]^{\frac{1}{3}} \quad (3.15)$$

Equation (3.15) is valid for all capillaries satisfying the condition :

$$\infty \geq \frac{V}{R^3} \geq 250$$

where V is the volume of the mercury drop (cc). Usual polarographic capillaries satisfy the above conditions (around 20μ to 200μ in radius). The mass flow rate of mercury is subjected to the second correction :

$$m = k (h - h_b) \quad (3.16)$$

where h = applied pressure on the mercury drop (cm of mercury)

h_b = correction term for back pressure

k = a constant depends on the capillary given by

Poiseuille's formula as :

$$k = \frac{\pi R^4 \rho_{Hg}^2 g}{8 \eta L} \quad (3.17)$$

and η = viscosity of mercury (poise)

L = length of the capillary (cm)

With a growing spherical drop of radius r , the back pressure due to interfacial tension $\frac{2 \gamma_i}{r}$ is continuously decreasing. The back pressure in this case is :

$$h_b = \frac{2 \gamma_i}{g r \rho_{Hg}} \quad (3.18)$$

Since r is continuously changing, it is assumed that the mercury flow rate is proportional to the effective pressure (difference between hydrostatic pressure and back pressure) :

$$\frac{m_1}{h - h_b} = \frac{m}{h} \quad (3.19)$$

or

$$m_i = \frac{d w_i}{d t} = m \left[1 + \frac{h_b}{h} \right] \quad (3.20)$$

where m_i = instantaneous mass flow rate of mercury

w_i = instantaneous mass of mercury of the hanging drop

If $h \gg h_b$, as is usually the case, equation (3.9) can be written as :

$$\frac{d w_i}{d t} \approx \frac{m}{1 + \frac{h_b}{h} + \frac{h_b^2}{h^2}} \quad (3.21)$$

Assuming the drop is spherical all the time, r can be written in terms of the weight as :

$$r_i = \left[\frac{3}{4 \pi \rho_{Hg}} \right]^{\frac{1}{3}} w_i^{\frac{1}{3}} \quad (3.22)$$

Substituting equation (3.18) and (3.22) into equation (3.21), it becomes :

$$\frac{d w_i}{d t} = \frac{m}{1 + s w_i^{\frac{1}{3}} + s^2 w_i^{\frac{2}{3}}}$$

$$\text{where } s = \frac{2 \gamma}{h g \rho_{Hg} \left[\frac{3}{4 \pi \rho_{Hg}} \right]^{\frac{1}{3}}}$$

Upon integration, mt can be obtained :

$$m t = w_i + \frac{3}{2} s w_i^{\frac{2}{3}} + 3 s^2 w_i^{\frac{1}{3}} \quad (3.23)$$

In order to find the average back pressure, let m_{av} and $h_{b_{av}}$ be the average values of m and h_b during the growth of a single drop under a mercury head h cm. Then,

$$m_{av} t = w \quad (3.24)$$

and

$$\frac{h - h_{b_{av}}}{h} = \frac{m_{av}}{m} = \frac{w}{m t} \quad (3.25)$$

From equation (3.25), it is found that :

$$\frac{w}{m \tau} = \frac{1}{1 + \frac{3}{2} \frac{s}{w} + \frac{1}{3} + 3 \frac{s^2}{w^2}}$$

And, it can be approximated as :

$$\frac{w}{m \tau} \approx 1 - \frac{3}{2} \frac{s}{w} + \frac{3}{4} \frac{s^2}{w^2} \quad (3.26)$$

$$= \frac{1}{h} \left[h - \frac{3 \gamma_i}{g R \rho_{H_2}} - \frac{1}{3} h \left(\frac{3 \gamma_i}{g R \rho_{H_2}} \right)^2 \right]$$

Comparing this to equation (3.25), it is clearly shown that :

$$h_{b,sv} = A + \frac{A^2}{3h} \quad (3.27)$$

where

$$A = \frac{3 \gamma_i}{g R \rho_{H_2}} \quad (3.28)$$

which differs from back pressure of a spherical drop by a factor of two-thirds.

Putting equation (3.15), (3.16), (3.17), and (3.27) back into equation (3.13), the final form will be :

$$2 \pi R \gamma_i = \alpha g k \left(h - h_{b_{av}} \right) \left(1 + \beta \right) t$$

$$\alpha = \frac{\rho_{Hg} - \rho}{\rho_{Hg}}$$

$$k = \frac{\pi R^4 \rho_{Hg}^2 g}{8 \eta L}$$

$$h_{b_{av}} = A + \frac{A^2}{3h}$$

$$A = \frac{3 \gamma_i}{g R \rho_{Hg}}$$

$$\beta = 3.680 R \left(\frac{\alpha g}{2 \pi R \gamma_i} \right)^{\frac{1}{3}}$$

The above equations were used in calibration of the radius of the capillary tube and calculation of the interfacial tensions from drop time measurement. Equations were programmed in a computer using Modified Regula Falsi method in solving the equations. (See Appendix).

3.5. ELECTROCAPILLARY EXPERIMENTS WITH AQUEOUS SOLUTION

3.5.1. CHEMICALS

- 1) Potassium Nitrate and Potassium Bromide from Mallinckrodt Inc., Paris, Kentucky 40361.
- 2) Didodecyl Dimethyl Ammonium Nitrate (DDAN), it was prepared in the laboratory from didodecyl dimethyl ammonium chloride (DDAC), Onyx Chemicals, Jersey City, NJ.07302. Silver nitrate was dissolved in a 50/50 mixture of ethyl alcohol and distilled water. DDAC was also dissolved in distilled water. Both solutions were heated and then mixed with stirring. Silver chloride precipitate was filtered out. Solution was evaporated until almost dry. Then, DDAN was recrystallized three times in hexane. The crystal obtained was about 100% pure.
- 3) Aerosol OT, sodium dioctyl sulfosuccinate, from American Cyanamid Co., Wayne, NJ.07470, 25% active.
- 4) Sarkosyl O, oleoyl sarcosine, is a high molecular fatty acid in which the hydrocarbon chain is interrupted by an amidomethyl group (molecular weight ~ 350). It was from Ciba Geigy Corp., Greensboro, NC.27409.
- 5) Cetyltrimethylammonium Bromide (CTAB), Myristyltrimethylammonium Bromide (MTAB), and Dodecyltrimethylammonium Bromide (DTAB), from Aldrich Chemical Co., Milwaukee, Wis. 53233.
- 6) Cetyldimethylethylammonium Bromide (CDME), from Onyx Chemical, Jersey City, NJ.07302.
- 7) Didodecyldimethylammonium Bromide (DDAB), from Eastman Kodak Co., Rochester, NY.14650. All the cationic bromide surfactants were purified by recrystallization at least three times in n-hexane and drops of 200-proof ethanol.

3.5.2. RESULTS

The interfacial tensions of Hg/water, Hg/ethanol, and Hg/benzene were measured using pendant drop method (59). Then, the drop times of mercury into the above solutions were recorded with known hydrostatic height. The radius of the capillary tube was calculated using equations in section 3.4. The radius was found to be 2.2778×10^{-3} cm, with an error of less than 1%. Cathetometer was used to determine the hydrostatic height and it was kept constant for all experiments.

0.01N Potassium Nitrate solution was used as the electrolyte solution and also as the reference electrocapillary curve for three surfactants, DDAN, Aerosol OT and Sarkosyl O. They were dissolved in the electrolyte solution at different concentrations. The applied potential was from -1.50V to 0.50V. Drop times were the average of five or more consecutive drops (at the order of 15 to 20 seconds/drop). After calculation, as shown in section 3.4, the interfacial tension was plotted against potential in Figure 3.4, 3.6, and 3.8 for Sarkosyl O, Aerosol OT, and DDAN respectively. The interfacial pressure versus potential for those surfactants were also plotted in Figure 3.5, 3.7, and 3.9. The interfacial pressure, π , is defined as :

$$\pi = \gamma^0 - \gamma_i \quad (3.29)$$

where γ^0 = interfacial tension of the supporting electrolyte

γ_i = interfacial tension of the electrolyte solution with surfactant at same applied potential

A homologous series of quaternary ammonium surfactants were also used, namely, DTAB, MTAB, CTAB, and CD¹⁴AE. Due to the availability of the surfactants in the form of bromide ions, supporting electrolyte solution was changed to 0.1N Potassium Bromide. The surface tensions of these cationic bromide surfac-

tants in 0.1N KBr were measured at 25 °C using a mica-blade and was plotted in Figure 3.10. The interfacial tension versus potential were plotted in Figure 3.11, 3.13, 3.15, and 3.17 while the interfacial pressure curves were shown in Figure 3.12, 3.14, 3.16 and 3.18. DDAB precipitated out in 0.1N KBr solution and no measurement was able to be done.

3.5.3. DISCUSSION

- 1) All the electrocapillary curves with surfactant showed a plateau shape rather than parabolic. No sharp maximum was found.
- 2) Cationic/anionic surfactants at 1:1 molar ratio precipitated out in the potassium nitrate electrolyte solution upon mixing. It gave back exactly the same curve as the pure electrolyte solution as if there was no surfactant.
- 3) Figure 3.4 shows the electrocapillary curves of Sarkosyl O. The top curve is the 0.01N Potassium Nitrate electrolyte solution alone. The electrocapillary maximum is at around -0.45V. The amphoteric surfactant was adsorbed at the dropping mercury electrode at moderate cathodic and anodic potentials (-1.00V to 0.00V) as accompanied by a lowering of interfacial tension from the top curve. At more extreme potentials, there is an increase in competition with the much more prevalent water dipoles and with the coulombically attracted ions from the supporting electrolyte, eventually displacing the surfactant. Therefore, the curve of pure electrolyte merges with those containing surfactant at extreme potentials. Adsorption is easier to visualize by plotting the interfacial pressure versus potential. From Figure 3.5, the pressure curves are parabolic. The amphoteric surfactant starts being adsorbed at around 0.0V and the pressure increases as the potential is decreasing. After reaching a maximum at around -0.50V, pressure decreases as potential is lowered and eventually drops back to zero at -1.80V where the surfactant is

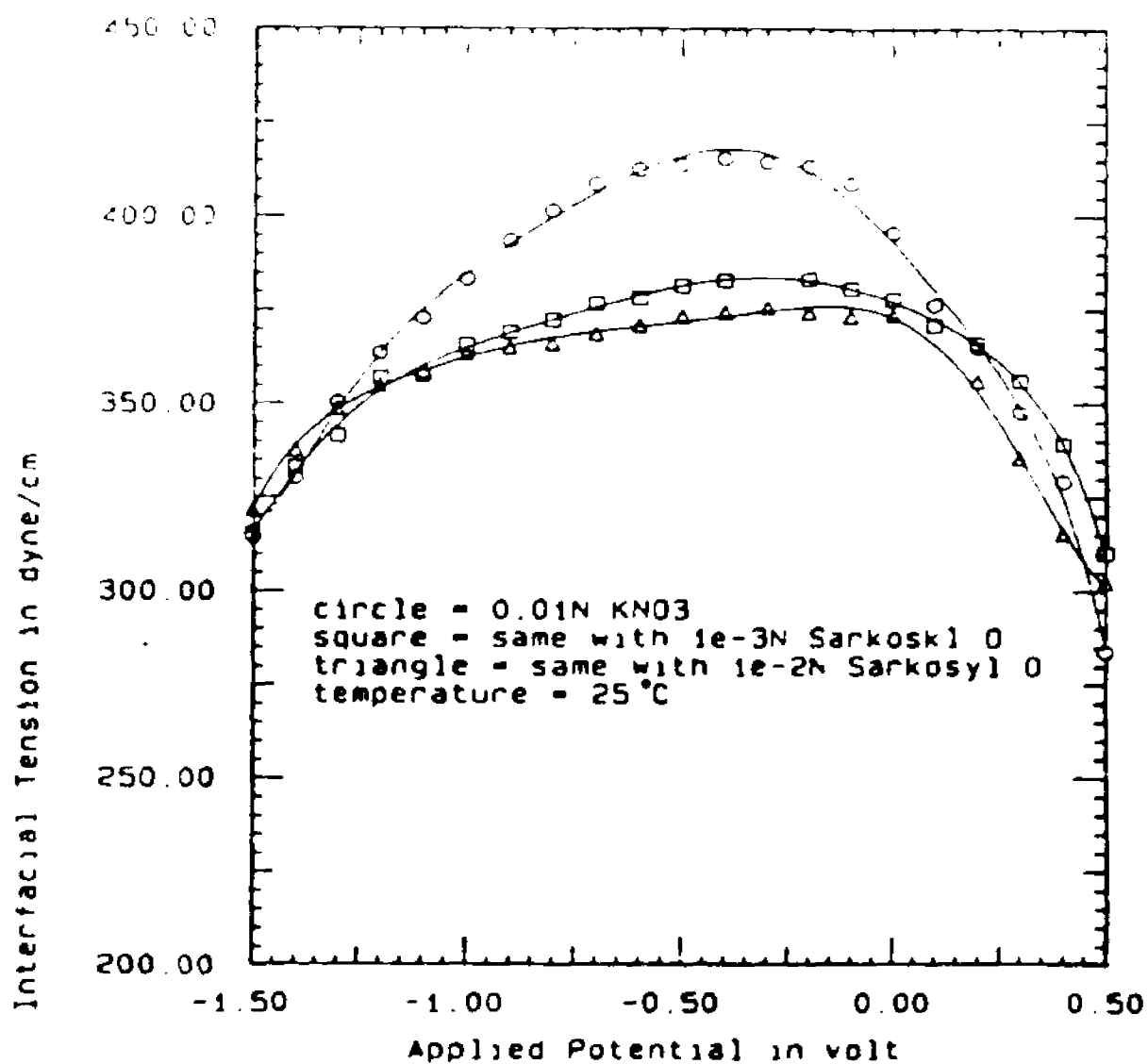


Figure 3.4 Electrocapillary curves of Sarkosyl O in 0.01N KNO₃

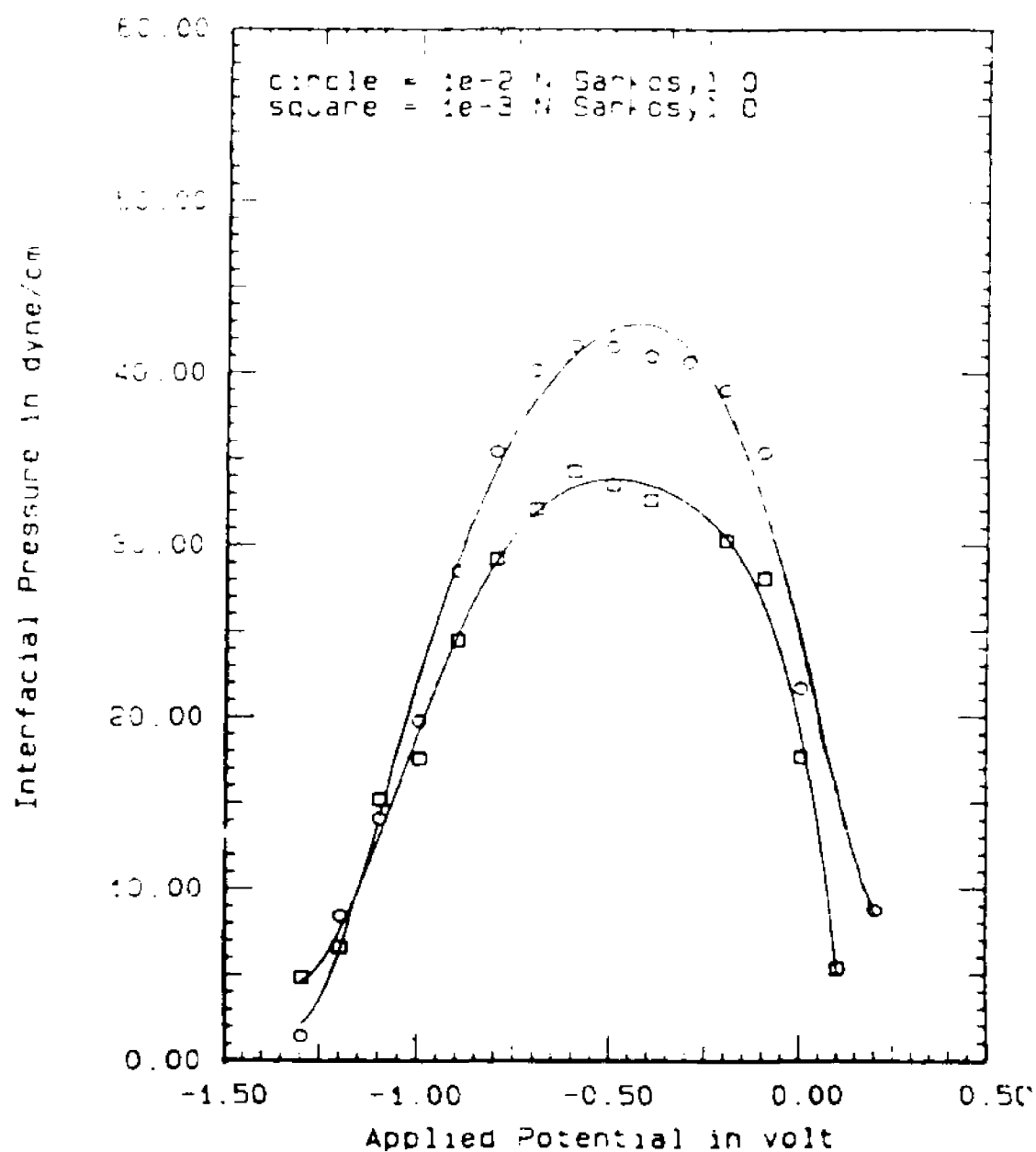


Figure 3.5 Interfacial pressure curves of Sarkosyl O from electrocapillary experiment

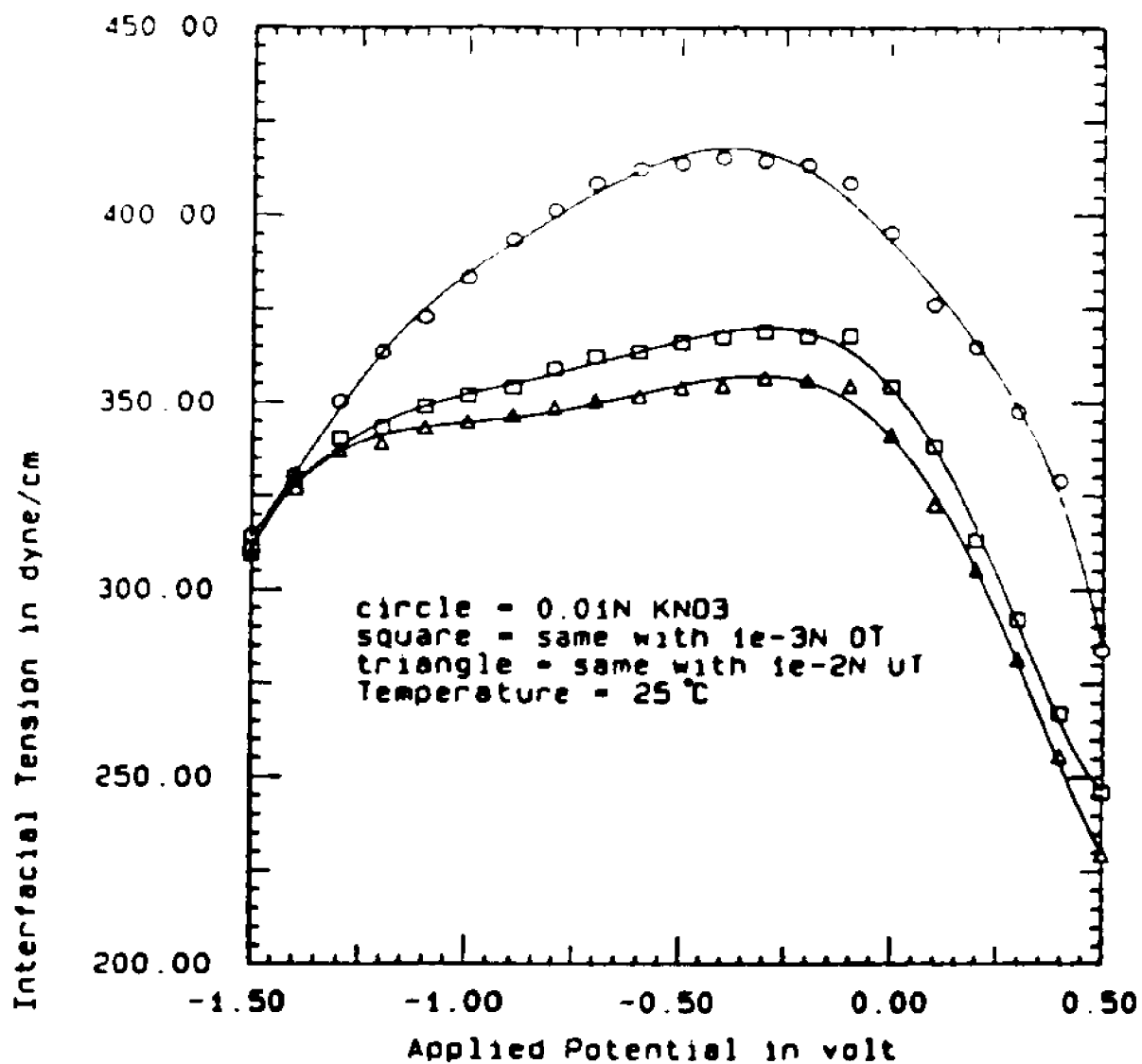


Figure 3.6 Electrocapillary curves of Aerosol OT in 0.01N KNO₃

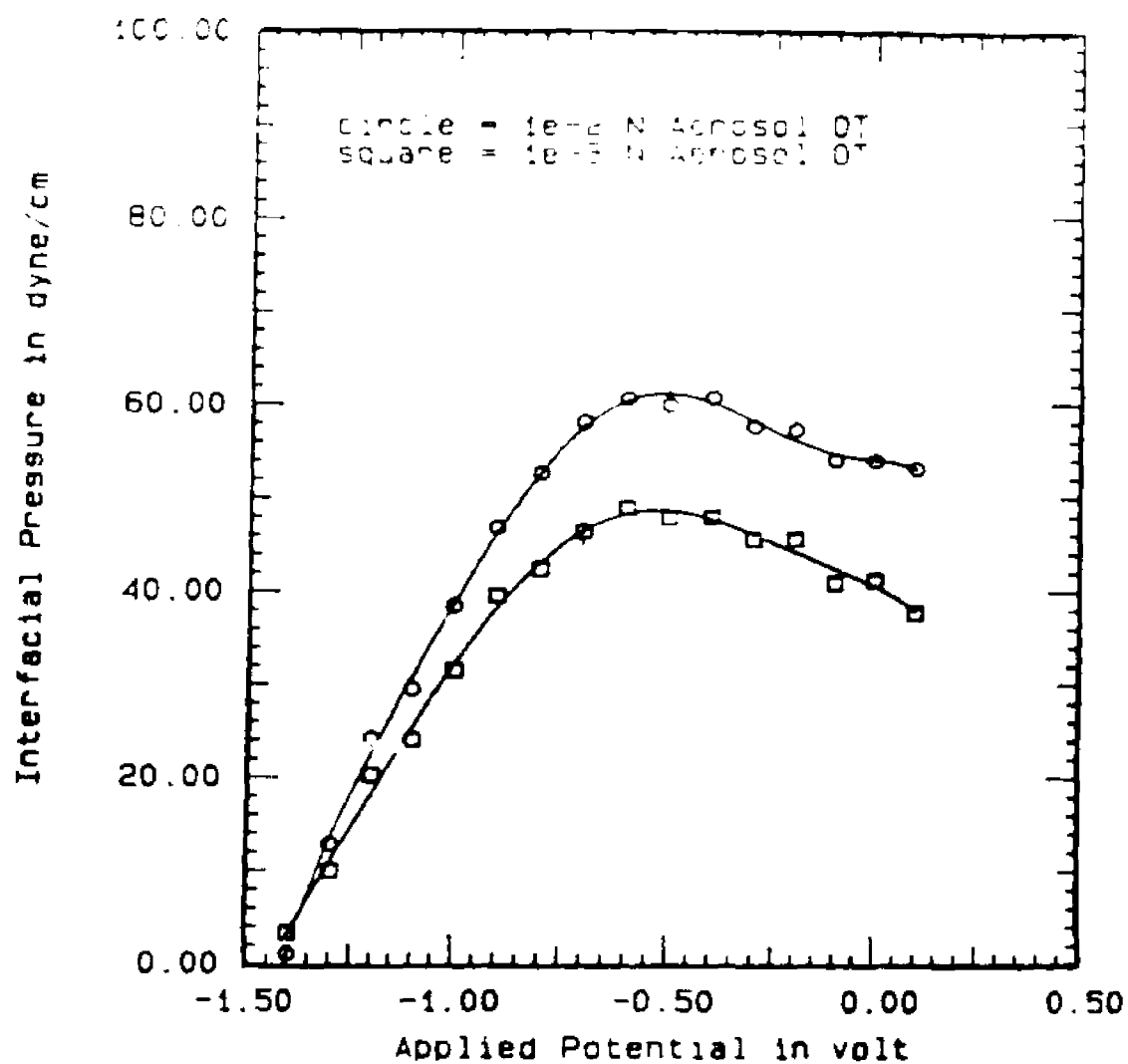


Figure 3.7 Interfacial pressure curves of Aerosol OT from electrocapillary experiment

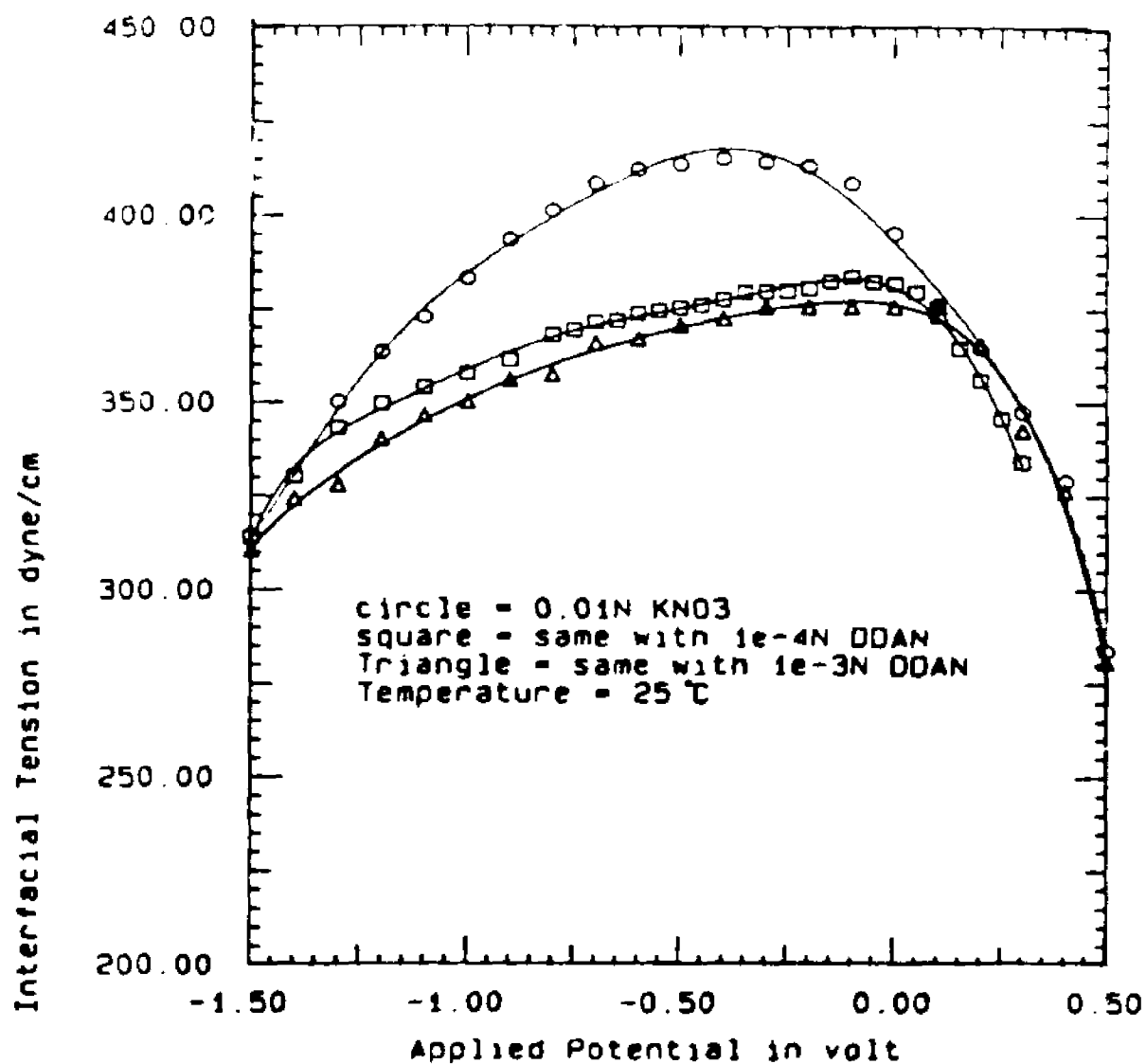


Figure 3.8 Electrocapillary curves of Didodecyl Dimethyl Ammonium Nitrate in 0.01N KNO₃

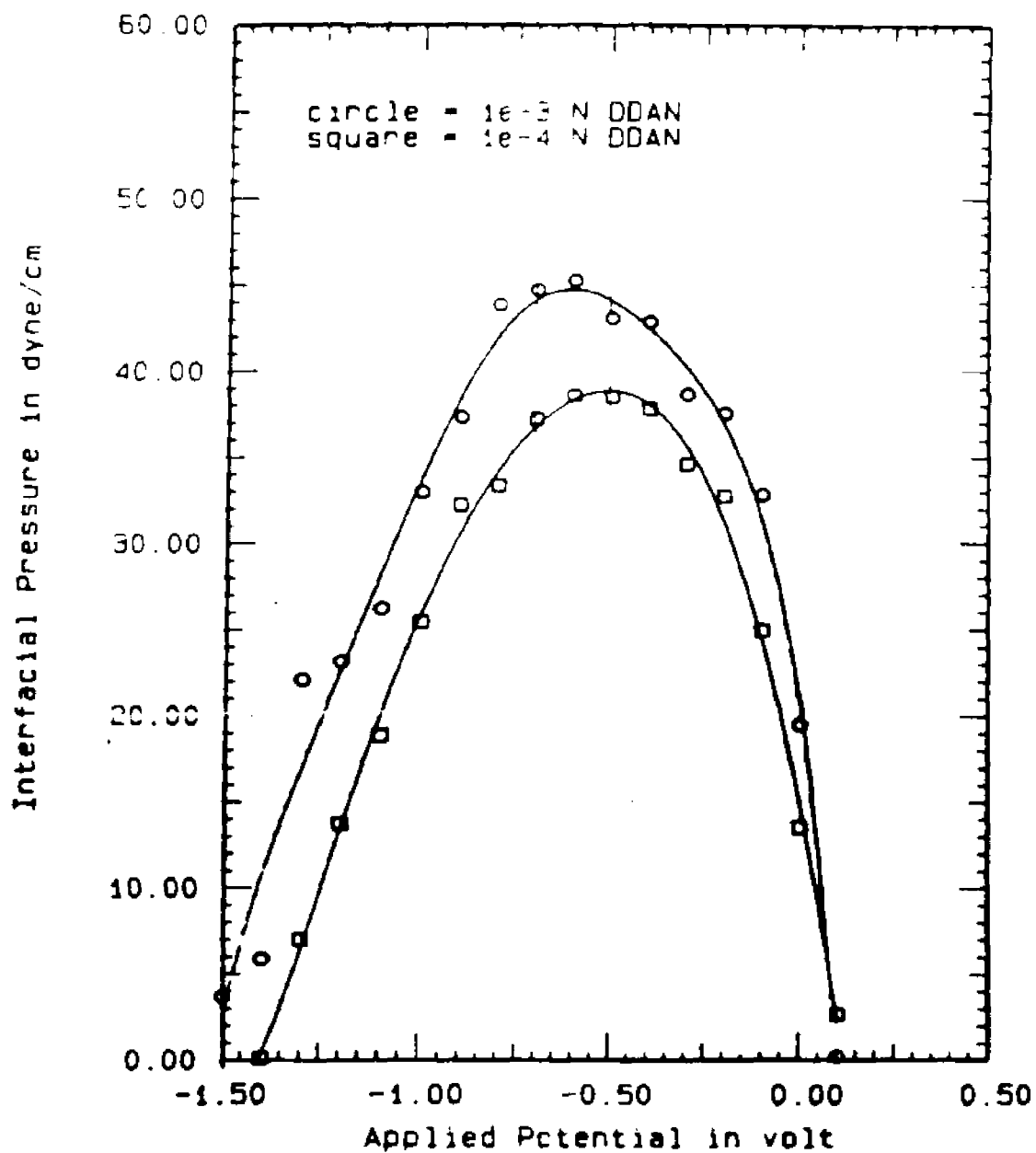


Figure 3.9 Interfacial pressure curves of Didodecyl Dimethyl Ammonium Nitrate from electrocapillary experiment

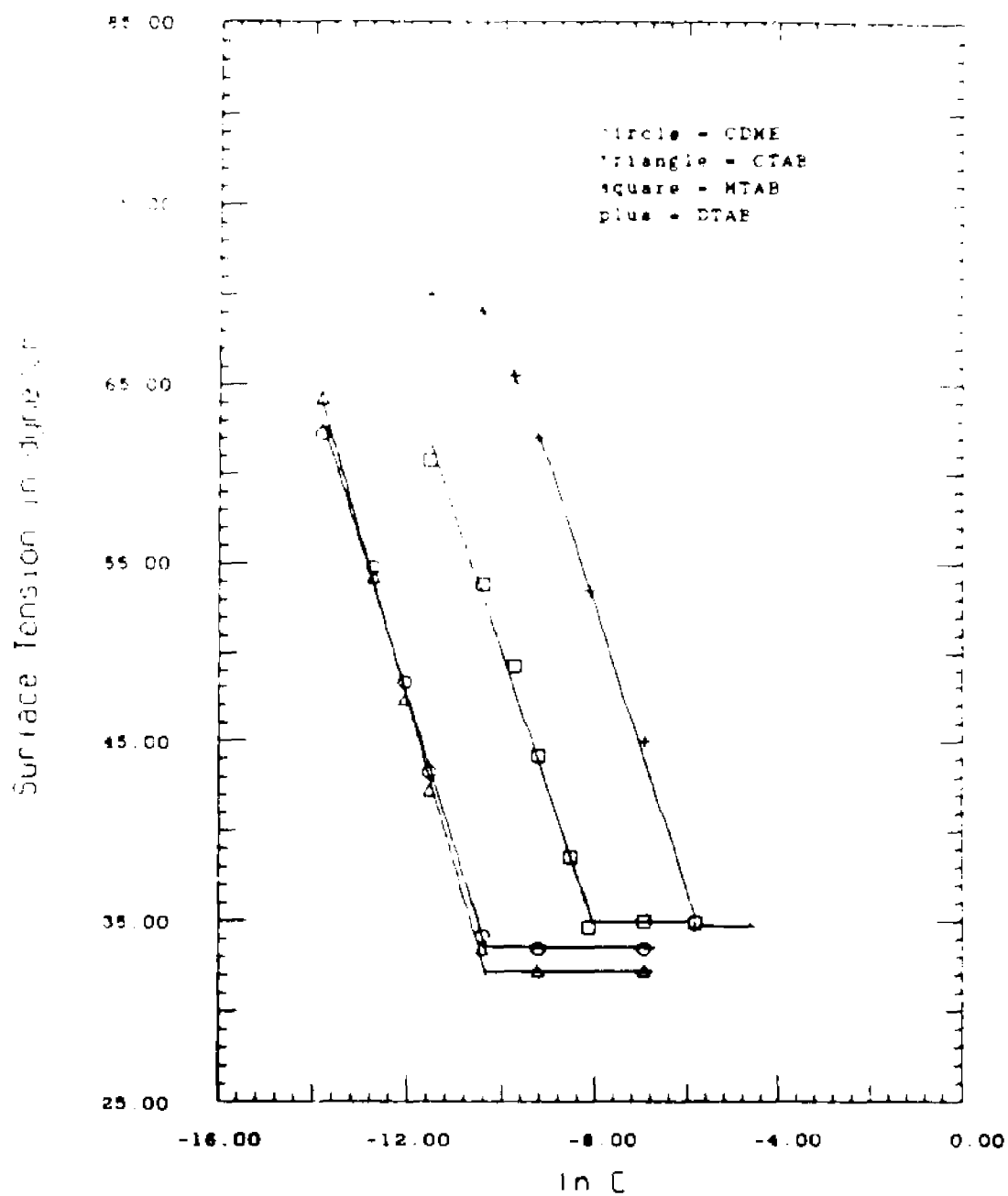


Figure 3.10 Surface tensions of quaternary ammonium bromide in 0.1N KBr solution

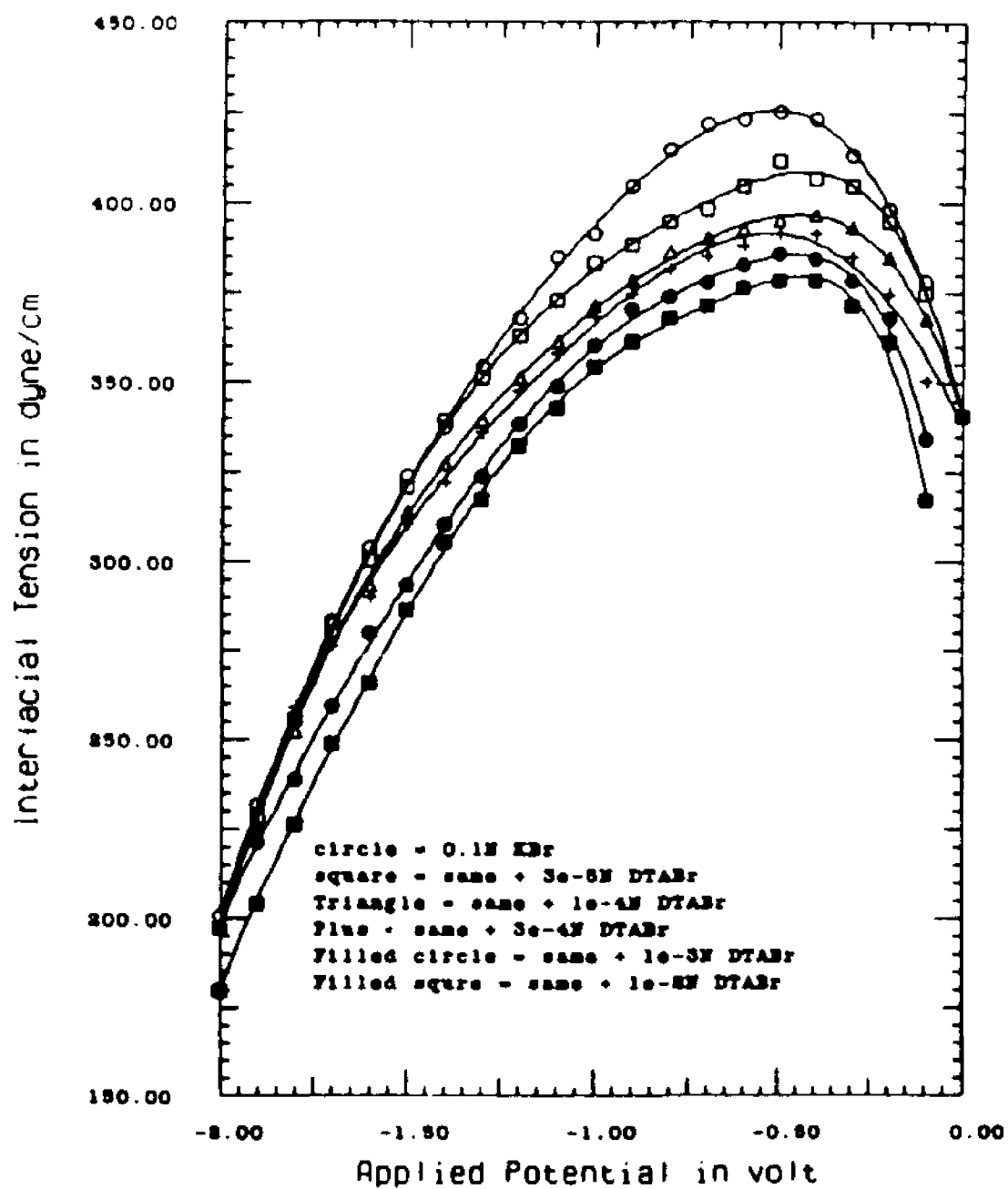


Figure 3.11 Electrocapillary curves of Dodecyltrimethylammonium Bromide in 0.1N KBr

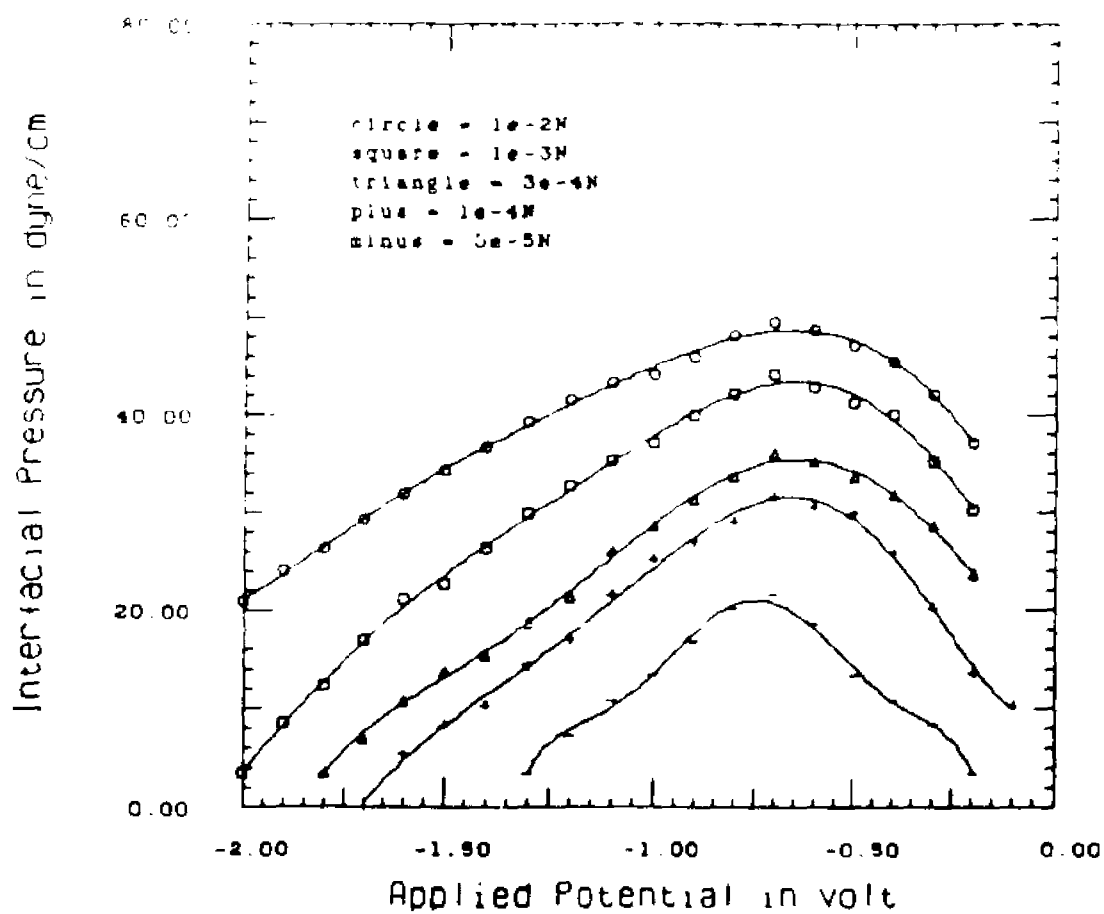


Figure 3.12 Interfacial pressure curves of Dodecyltrimethylammonium Bromide from electrocapillary experiment

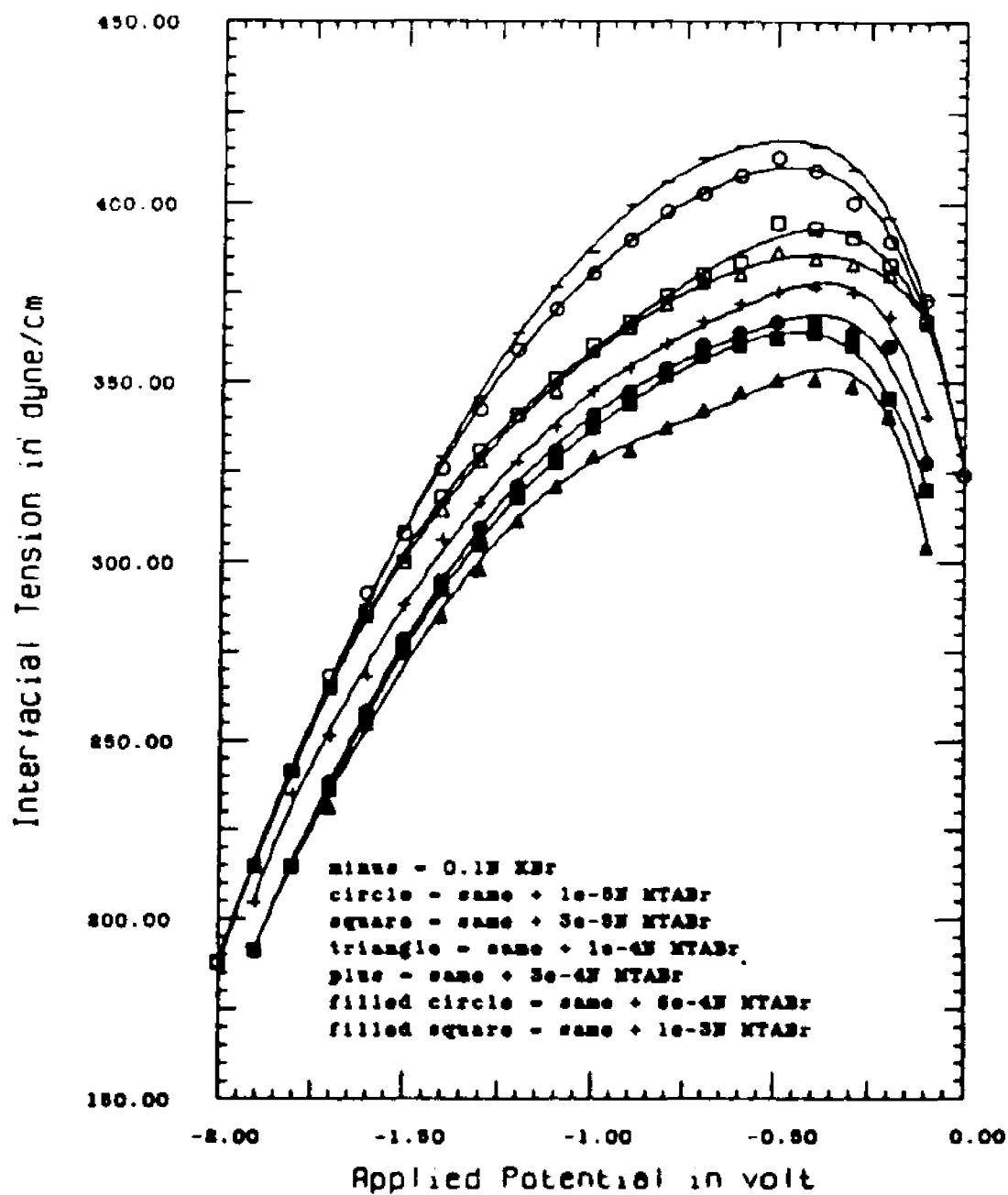


Figure 3.13 Electrocapillary curves of Myristyltrimethylammonium Bromide in 0.1N KBr

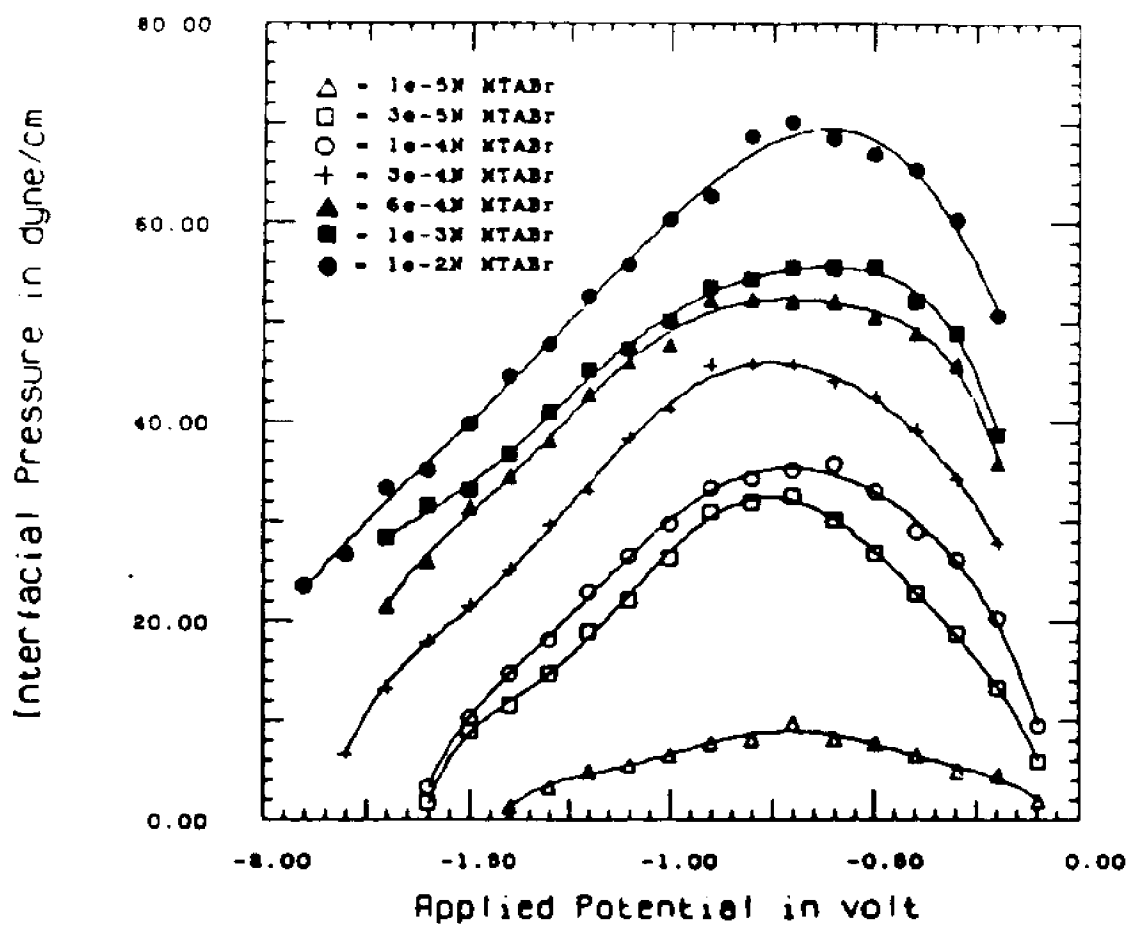


Figure 3.14 Interfacial pressure curves of Myristyltrimethylammonium Bromide from electrocapillary experiment

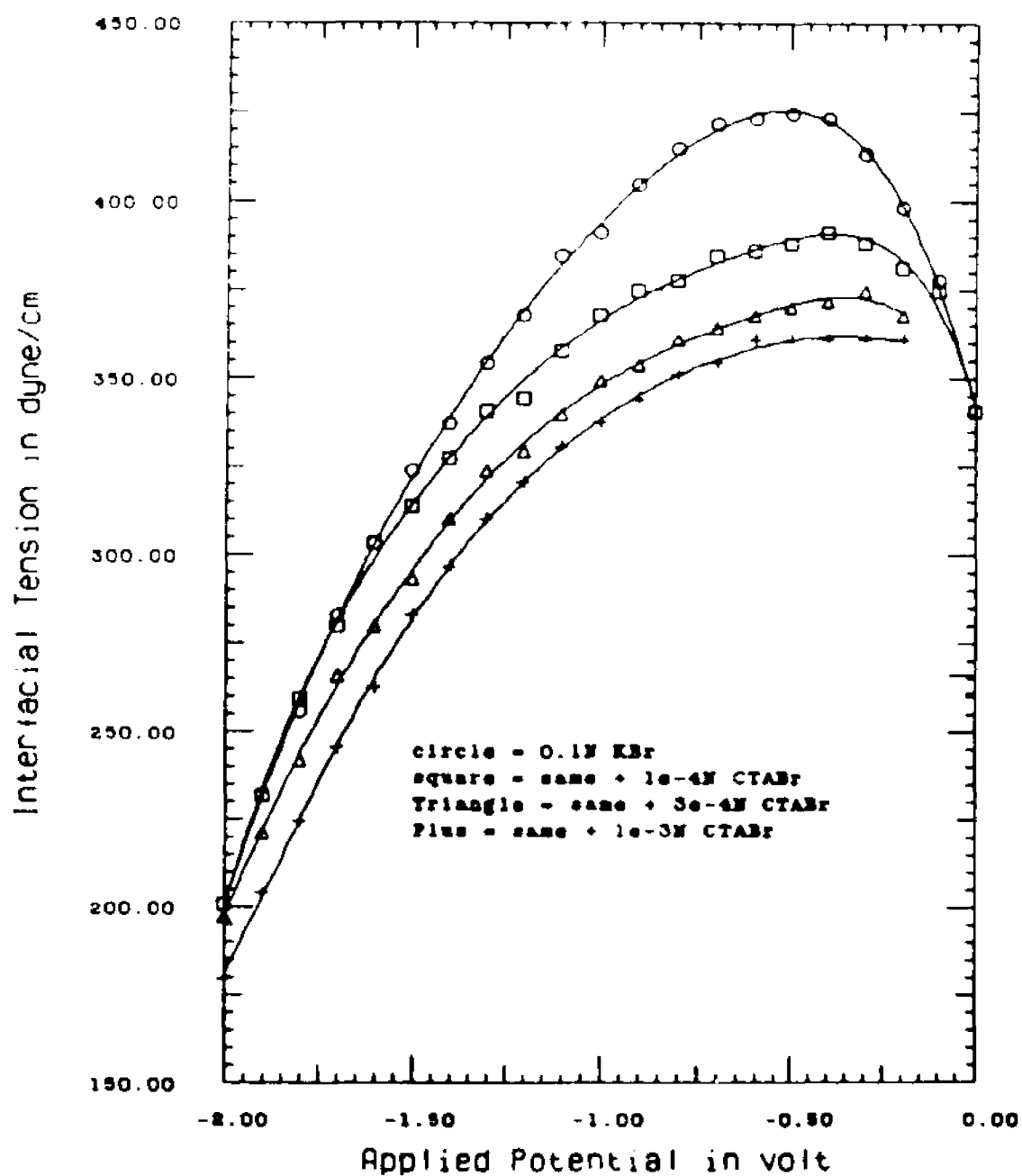


Figure 3.15 Electrocapillary curves of Cetyltrimethylammonium Bromide in 0.1N KBr

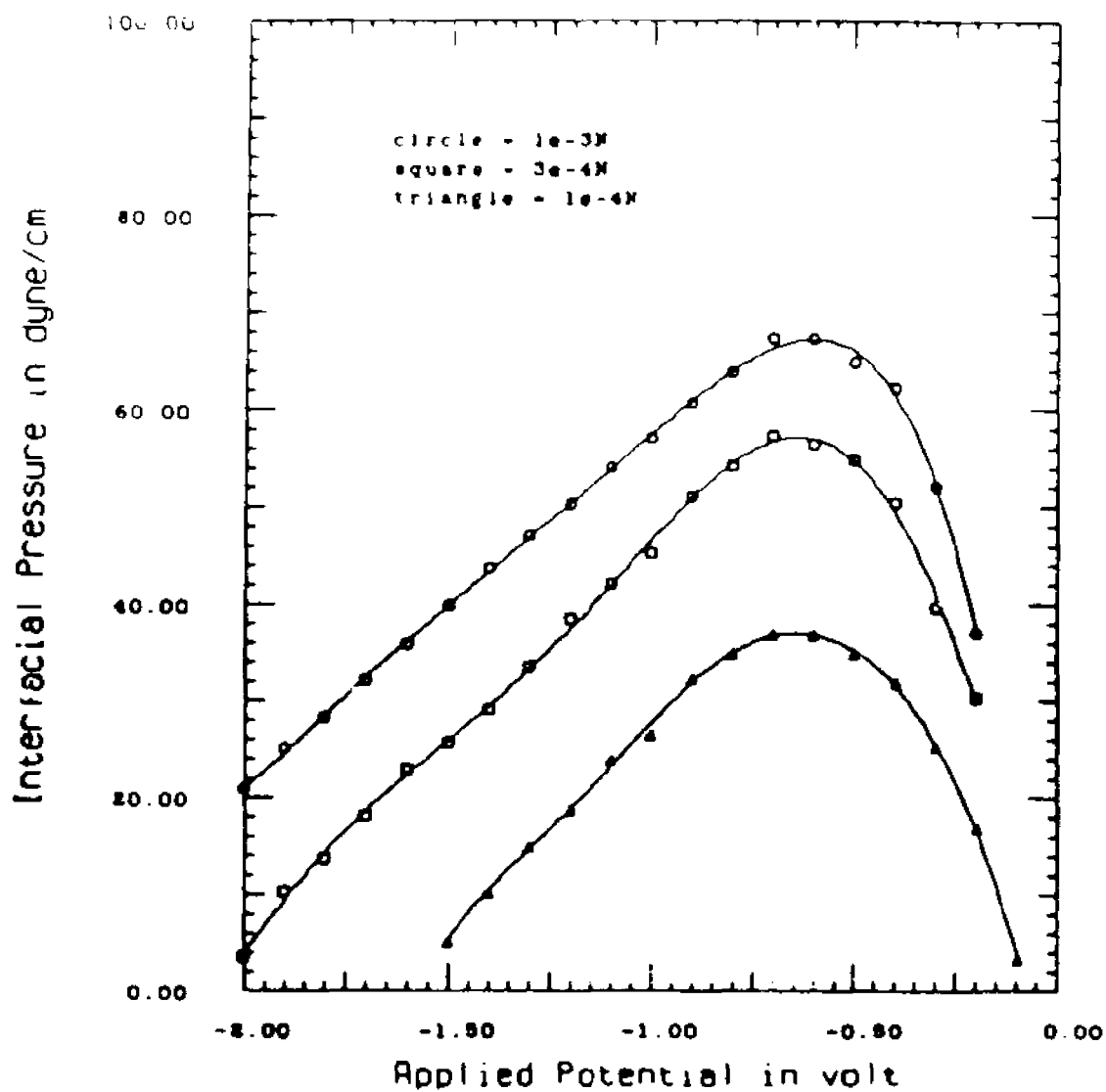


Figure 3.16 Interfacial pressure curves of Cetyltrimethylammonium Bromide from electrocapillary experiment

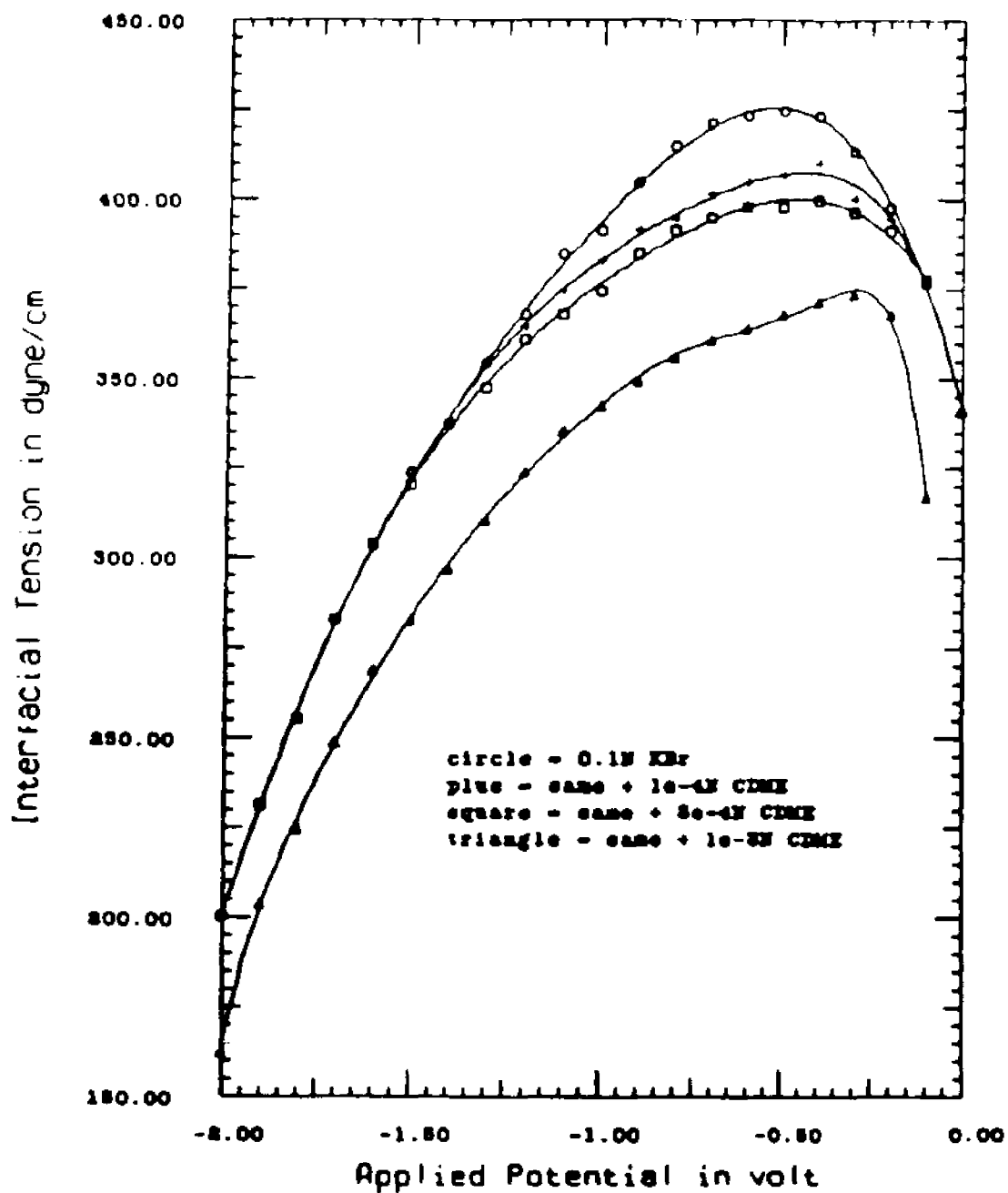


Figure 3.17 Electrocapillary curves of Cetyldimethylethylammonium Bromide in 0.1N KBr

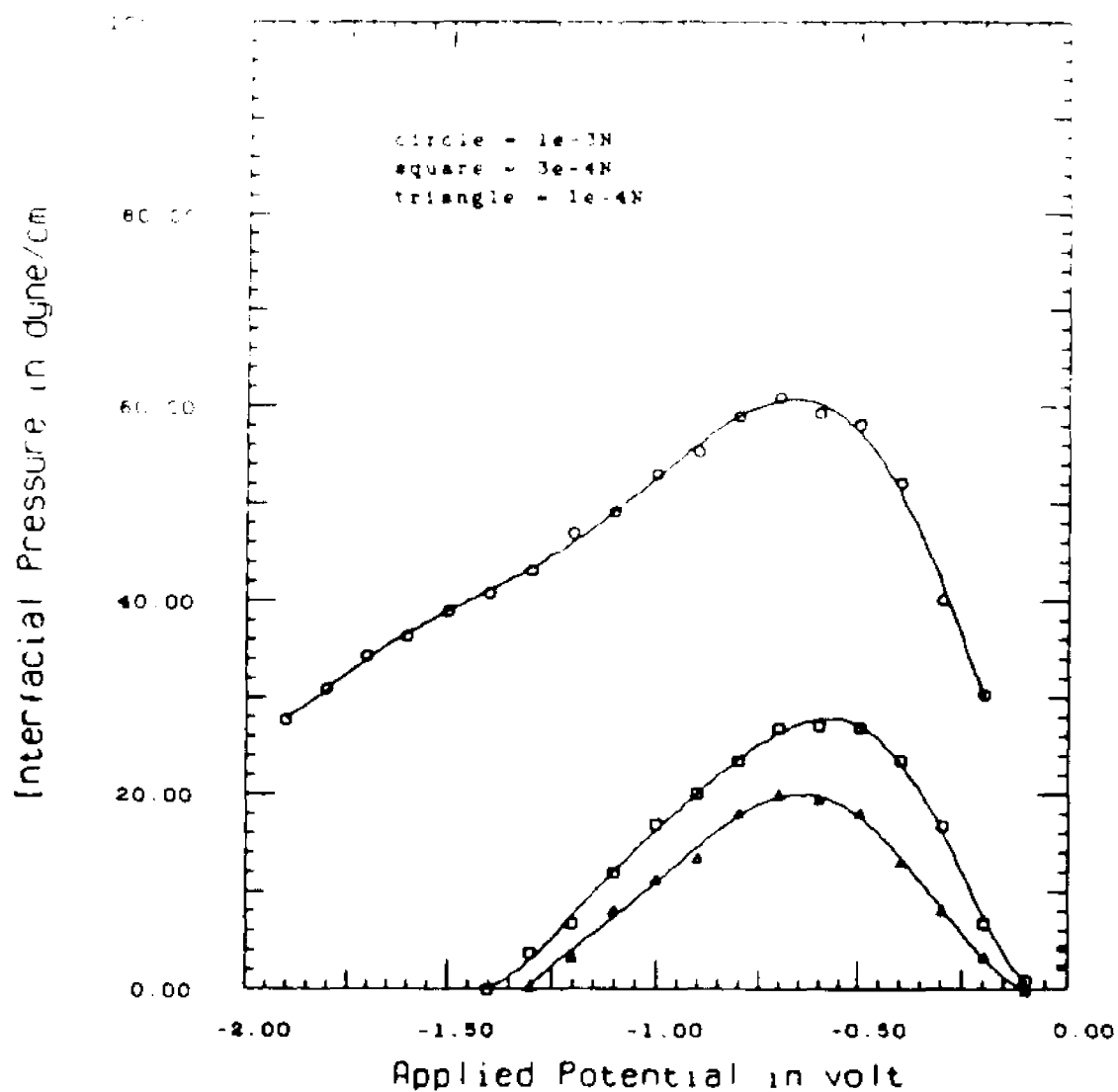


Figure 3.18 Interfacial pressure curves of Cetyltrimethylammonium Bromide from electrocapillary experiment

completely desorbed from the mercury. Maximum pressure, which corresponds to maximum adsorption occurs at around -0.50V which is in the area of the point of zero charge. At that particular potential, the amphoteric surfactant has basically no competition with the supporting electrolyte and gives the maximum pressure. As the mercury surface is charged, electrolyte is attracted and less surfactant can be absorbed. This amphoteric surfactant behaves as if it were non-ionic. And, the higher concentration of the surfactant gives a higher maximum pressure as expected.

- 4) Figure 3.6 shows the electrocapillary curves of Aerosol OT, an anionic surfactant. It starts being adsorbed at -1.40V , as interfacial tension is lowered and even as the mercury surface is negatively charged. The capillary curves of the surfactant reach a plateau and then decrease as potential increases. However, they never merge with the supporting electrolyte curve as the Sarkosyl O, indicating no desorption at the extreme positive potential. Again, the interfacial pressure was plotted versus the potential in Figure 3.7. Pressures start increasing from zero at -1.40V . After reaching a maximum, the pressures level out, instead of decreasing back to zero as in the case of Sarkosyl O. As potential increases, more anionic surfactant is adsorbed. Maximum pressure again is at around the point of zero charge. Further increase in potential after the PZC does not increase the pressure. Instead, it remains relatively constant throughout the anodic branch. Positively charged mercury attracts both the nitrate ions and the anionic surfactant. Coulombic attractive force of the two is equal so that the pressure remain constant. And, the anionic surfactant stays at the interface as opposed to Sarkosyl O in the anodic branch due to the difference in the electrical charge of the surfactants. The pressure curves actually are similar to the monolayer compression curves of fatty acid at water-air interface (60). In one case, the increase in pres-

sure is due to the compression while in the other, it is achieved by increasing the potential.

- 5) The electrocapillary curves of DDAN were plotted in Figure 3.8. Adsorption of this cationic surfactant starts at 0.10V, where mercury is positively charged. Nevertheless, adsorption occurs at moderate cathodic and anodic potentials and the curves merge with the one of the supporting electrolyte at high negative potential. The interfacial pressures were plotted in Figure 3.9. Surprisingly, instead of behaving oppositely to Aerosol OT, the curves are parabolic. This behaviour was observed by other authors too (61). Apparently, there is no reason for the surfactant to desorb at the cathodic branch and the curves are not mirror images of the anionic surfactant as expected. Further investigation has to be carried on.
- 6) In order to investigate the phenomenon of the cationic surfactant, a homologous series of quaternary ammonium compounds were used. The homologous series of quaternary ammonium compound was available only as bromide salt. The supporting electrolyte was switched from Potassium Nitrate to Potassium Bromide to eliminate the effect due to the difference in anion. The surface tensions of these cationic surfactants in 0.1N KBr (water/air interface) were measured and plotted versus $\ln C$, the concentration as shown in Figure 3.10. From their surface tension curves, their critical micelle concentrations are 3.0×10^{-3} mole/l, 3.0×10^{-4} mole/l, 3.2×10^{-5} mole/l, and 3.2×10^{-5} mole/l for DTAB, MTAB, CTAB, and CDME respectively. It is well known that salt in general decreases the CMC of ionic surfactants. Comparing the surface tension curves of DTAB, MTAB, and CTAB, it was found that increasing the chain length of the main branch decreases the surface tension (at the same concentration) and the CMC dramatically. However, the addition of a methyl group in the side chain did

not change the CMC nor the surface tension as it did in the main chain (i.e., for CTAB and CDME). Gibbs equation defines the adsorption isotherm for the two dimensional ideal case as :

$$\Gamma_2^1 = - \frac{1}{RT} \frac{d \gamma}{d \ln C} \quad (3.30)$$

where Γ_2^1 = surface excess

γ = surface tension in dyne/cm

C = bulk concentration of the surfactant

R = gas constant

T = absolute temperature

The area/molecule, σ , for the surfactant can be calculated as the reciprocal of Γ_2^1 as :

$$\sigma = \frac{R T}{d \pi / d \ln C} \quad (3.31)$$

where π is the surface pressure. Linear-regression was used to calculate $\frac{d \pi}{d \ln C}$. All four surfactants were found to have σ close to $50 \text{ \AA}^2/\text{molecule}$ as they all have similar slopes in Figure 3.10 (i.e. same $\frac{d \gamma}{d \ln C}$ values). This σ value agrees with those found by Davies (62) from monolayer compression experiments of Stearyltrimethylammonium ions. This proves that the surfactants are standing straight up at the water/air interface since increasing the chain length of the surfactant does not increase the area occupied by the molecule.

- 7) For the electrocapillary experiments, the interfacial tensions were plotted in Figure 3.11, 3.13, 3.15 and 3.17 while the interfacial pressures were plotted in Figure 3.12, 3.14, 3.16, and 3.18 versus the applied potential for DTAB, MTAB, CTAB and CDME respectively. From the electrocapillary curves, all the cationic surfactant curves merge with the pure Potassium Bromide

curve at high negative potentials. The electrocapillary maximum shifts slightly to the more anodic polarization shows primary adsorption of the cationic surfactant. And, the downward displacement of the curves for more concentrated solutions indicates a positive adsorption of the surfactant even at electrocapillary maximum.

- 8) The interfacial pressure curves are more or less parabolic in shape for the cationic surfactants. In, particular, MTAB pressure curves were used to construct the adsorption isotherm for mercury/solution interface using equation 3.31 at fixed applied potentials. A computer program using linear-regression method was used to fit the data from Figure 3.14 for MTAB to form a polynomial. Then, the derivative of π with respect to $\ln C$ was calculated and substituted back into equation 3.31. This way, a continuous curve of π versus σ was able to be constructed. The isotherms at -0.30V, -0.50V, -0.70V and -0.90V, were plotted in Figure 3.19. At -0.30V and -0.50V (positively charged interface), the isotherms are of a condensed liquid film type. There is a region of gradual transition to a linear π - σ behavior. However, the compressibility is relatively low and the packing of the surfactant molecules is close. For -0.7V and -0.90V (negatively charged interface), the π - σ plot is more linear and the transition is more critical. The adsorbed surfactant film is very rigid and very low in compressibility. They are known as solid films. The value of σ was close to $40\text{\AA}^2$ in all cases versus $50\text{\AA}^2$ found by surface tension measurement. This may suggest that the adsorbed surfactant may be more closely packed at mercury/liquid interface than at air/liquid interface. Similar adsorption isotherms were found for the other cationic surfactants.

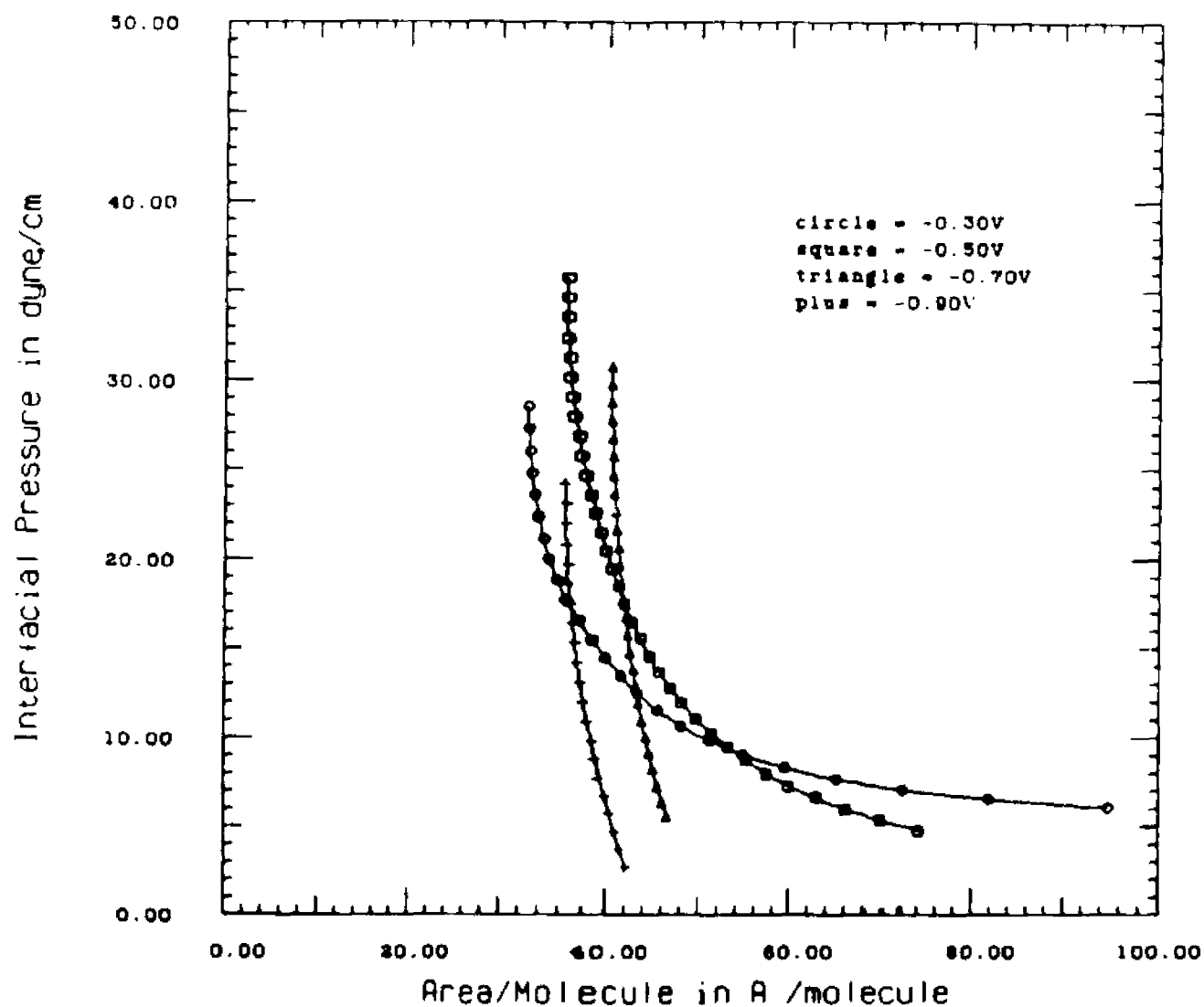


Figure 3.19 Adsorption isotherm of Myristyltrimethylammonium Bromide in 0.1N KBr solution at mercury/liquid interface at fixed applied potential

3.5.4. CONCLUSION

It was concluded in the previous chapter that surface charge of the solid is the major factor in determining whether a solid will be dewetted or not. In order to investigate the electrostatic effect on adsorption of surfactant, electrocapillary method was chosen to study the adsorption of ionic surfactants at solid/liquid interface. Mercury was used so that the interfacial charged could be varied from positive to negative.

From electrocapillary experiments, it was found that Sarkosyl O, an amphoteric surfactant, adsorbed only at moderate cathodic and anodic potentials in the supporting electrolyte solution. For the anionic surfactant, adsorption occurs mostly when the mercury is positively charged as expected. It was a surprise that cationic surfactants appeared to be adsorbed at moderate potentials only as the amphoteric surfactant.

Further investigation using a homologous series of quaternary ammonium surfactants showed similar results. However, from the adsorption isotherm of Myristyltrimethylammonium Bromide, it was found that the adsorbed cationic surfactant film at positively charged mercury surface is of condensed liquid type. When mercury is negatively charged, the film is more condensed and a solid type of film is formed. This suggested that instead of desorption of the cationic surfactant at high negative potential, the adsorbed surfactant film changed from the condensed liquid type to a solid film. It is well known that anion tends to lose its hydration sheath more readily than a cation. Therefore, anionic surfactants may have more competition with anions than in the case of cationic surfactants with cations. More result will be presented in the next chapter about this matter.

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CHAPTER 4

SURFACE ENHANCED RAMAN SCATTERING SPECTROSCOPY

4.1. INTRODUCTION

Fleischmann and coauthors (1) published the first paper on the Raman spectroscopy (RS) of molecules adsorbed at a metal electrode under in situ electrochemical conditions. He obtained a laser Raman spectrum of a thick layer of mercurous halides formed from mercury plated on platinum. He then opened up a new field by reporting the Raman spectrum of pyridine adsorbed on a silver electrode under potentiostatic control in potassium chloride electrolyte solution (2). The intensity of the Raman spectrum of pyridine was enhanced (3,4) by at least five to six orders of magnitude over those from the scattering cross section of isolated molecules. This enhanced scattering intensity let one observe the surface Raman spectrum of a monolayer of adsorbed molecules. It is impossible to obtain a spectrum from a laser beam passing through the same number of molecules in a volume element of the bulk media.

Surface enhanced Raman scattering spectroscopy (SERS) is now a new spectroscopic technique which makes it possible to obtain vibrational spectra of molecules adsorbed on metal substrates under in situ conditions. SERS was studied at a silver working electrode of an electrochemical cell and it is ideal to obtain spectral information at a metal electrode/electrolyte interface. Even though silver and mercury are different substances, yet they are very similar in terms of surface properties. Because SERS gave very weak spectra at mercury/solution interface, silver was used. Nevertheless, the result was comparable to mercury. This serves as a technique to study the adsorption of molecules at a solid/liquid

interface.

Other methods for obtaining similar in situ spectral information at an electrode/electrolyte interface such as internal or external reflectance spectroelectrochemistry and ellipsometry are not as sensitive or specific as SERS. This great sensitivity results from a large inelastic scattering cross section. SERS is especially useful for molecules containing coordinating atoms (i.e. such as nitrogens with lone pairs). Calculations based on the number of molecules in a monolayer covered with end-on adsorption with respect to the number of molecules in a volume element encountered by the laser beam in solution indicated the enhancement factor of the electrode surface on the Raman scattering cross section of an isolated molecule is 10^5 to 10^6 (3,4,5). This anomalous increase of intensity of Raman scattering led to the name "Surface Enhanced Raman Scattering".

4.2. EXPERIMENTAL

A complete block diagram for SERS experimental set-up (6) is shown in Figure 4.1. 488 nm argon ion laser was used on a silver electrode which was made from a thick silver wire inserted in teflon for insulation. The laser beam was focused to a spot smaller than the silver wire. Then, the scattered light was collected with a spectrometer with a configuration of 90° angle collection geometry (Figure 4.2-a). The sum of the angle of incidence, ϕ_i , and the angle of observation, ϕ_s , is constant as 90° , and the angle of incidence was varied by rotating the electrode, which was on a X-Y-Z micropositioner. This is a conventional configuration which has the disadvantage that the angle of incidence or observation cannot be varied easily. Another alternative is the back scattering geometry (shown in Figure 4.2-b) in which the position of the laser can be rotated easily to change the angle of incidence. The SPEX Ramalog 1401 monochromator was

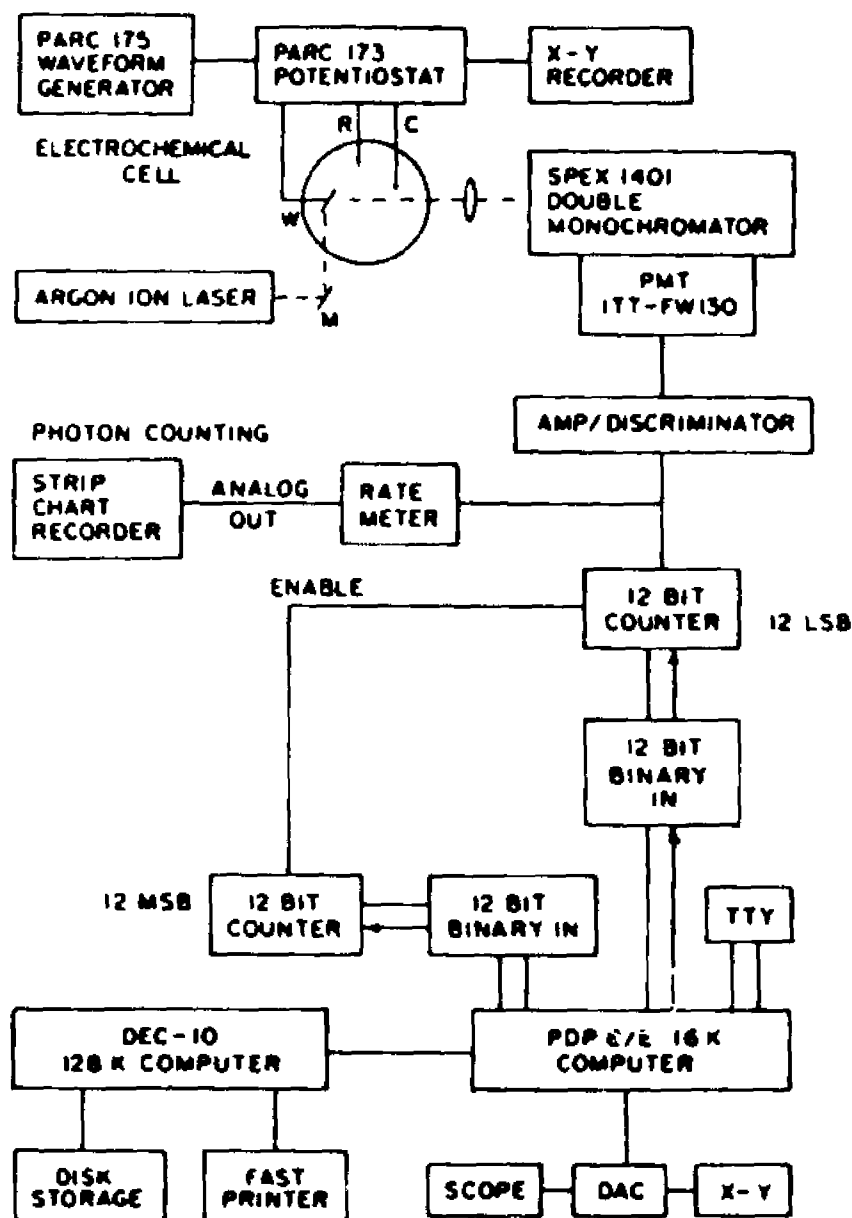


Figure 4.1 Block diagram of a complete computer interfaced spectroelectrochemical system for Surface Enhanced Raman Scattering

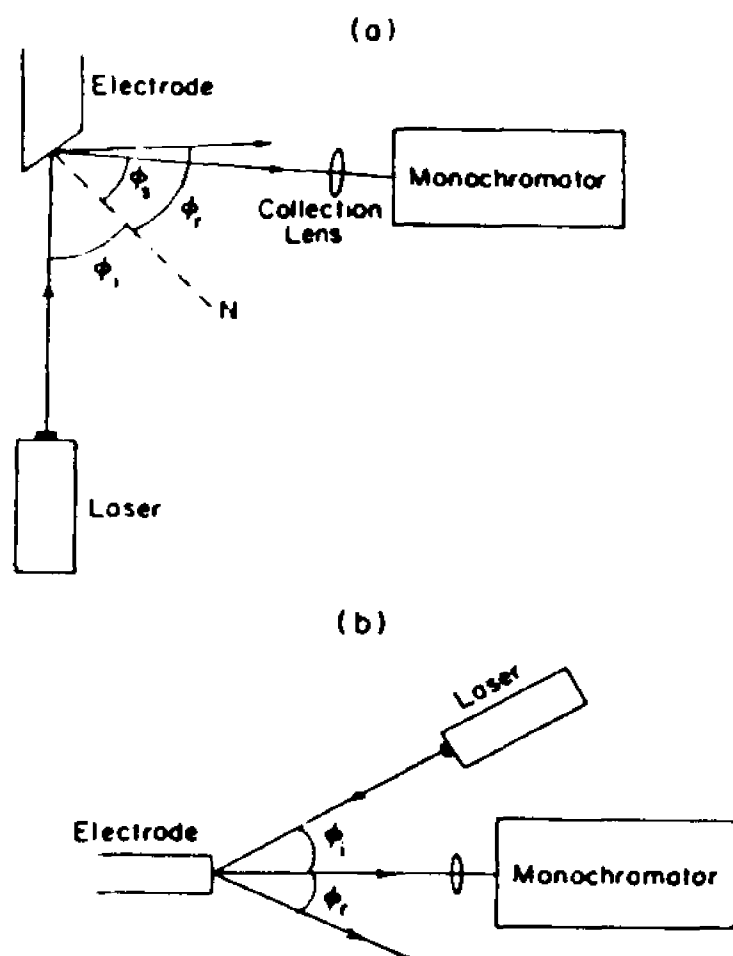


Figure 4.2 Scattering collection geometries
a) 90° mode b) back scattering mode

used. The electrochemical cell for SERS is shown in Figure 4.3. Both the bottom and one side of the cell were made with an optically flat quartz window. The working electrode potential was controlled with respect to a Luggin capillary reference electrode by a potentiostat that provided current through the counter electrode (platinum electrode).

Typical laser power at the electrode was 100 mW and the spectral bandpass was 2 to 5 cm^{-1} . Data files of 500 24-bit double precision data words (points) could be stored in the PDP-8/E. Eight storage buffers were available in the PDP-8/E. Mathematical manipulation such as smoothing, integrating, and subtraction of one 500-point spectrum from another could be accomplished in the minicomputer. A complete spectrum of 3000 double-precision points could be recorded continuously using six buffers. An intensified reticon diode array detector with optical multichannel analyzer (OMA) was used to obtain rapid data acquisition. A complete spectrum of 500 points can be obtained in millisecond to seconds.

4.3. SILVER ELECTRODE SURFACE PRETREATMENT AND ROUGHNESS

Van Duyne and co-workers (7,8) found that a polished silver electrode, without electrochemical pretreatment, gives an enhancement factor of 10^4 with pyridine at -0.6V vs. SCE. This enhancement on silver decayed below background when the electrode potential was shifted to 0.0V vs. SEC. The silver electrode showed a flat surface using scanning electron microscopy (SEM) after it was highly polished mechanically with 0.3 to 0.05 μm diameter particles of aluminum slurry. This indicated that the surface roughness was less than the resolution (250 Å) of the particular SEM technique used (9). Thus the roughness on the silver electrode at a scale larger than 250 to 500 Å only contributed a factor of, at most, 100 to the enhancement mechanism. In our experiment, Micropolish II, gamma alumina of 0.3 and 0.05 micron (from Buehler Ltd., Lake Bluff, IL) was

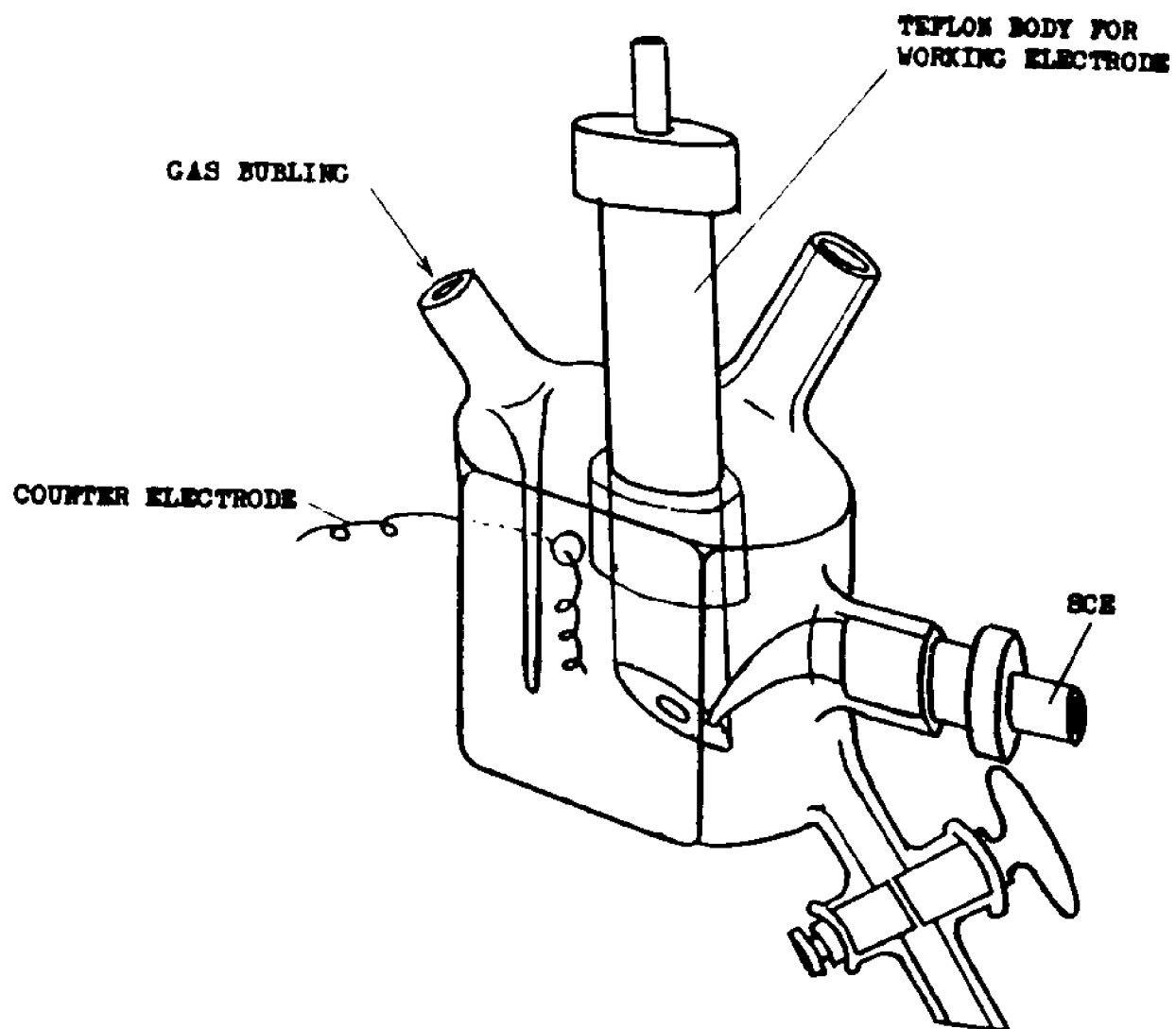


Figure 4.3 Electrochemical cell for Surface Enhanced Raman Scattering experiment

used to polish the silver electrode surface mechanically before electrochemical roughening.

The most intense Raman signal is found for a silver electrode when it is subjected to an oxidation/reduction cycle that forms silver chloride on anodization and reforms silver on cathodization. It can be done either by using a single double potential step or a triangular sweep with anodic potential limit of +0.3V vs. SCE. Above a maximum of 30 mC/cm², the signal intensity reaches a plateau and then decreases beyond 50 mC/cm² (3,5,7). Jeanmaire and co-workers (3) pretreated a highly alumina polished silver electrode using a double potential step pretreatment of -0.60 to +0.20V vs SCE and returning to -0.60V. Allowing 25.00 mC/cm² to flow through to the silver electrode, very intense Raman spectra for pyridine were observed, 30 to 100 fold more than in those roughened by the procedure of Fleischmann (2). Albrecht (4) obtained similar results using a single triangular sweep to pretreat the silver electrode.

4.4. NORMAL RAMAN SCATTERING SPECTROSCOPY

Myristyltrimethyl Ammonium Bromide (MTAB) from Aldrich Chemical Co., Milwaukee, Wisconsin 53233, was used as the cationic surfactant. It was purified at least three times by recrystallization in n-Hexane and drops of 200-proof Ethanol.

A normal Raman Scattering experiment was done in order to identify the surfactant later on in the Surface Enhanced Raman Scattering. The cell for Normal Raman is different from that used in SERS. The solution was put into a thin flat quartz cell instead. Monochromatic laser light (of a single frequency, μ_o) was shined to the bottom of the cell. Most of the light merely passed directly through the solution. Some of the light, i.e., about $\frac{1}{1000}$ of the incident intensity,

was scattered and collected (with a 90° angle configuration) by the double monochromator. This type of scattering contains both Rayleigh and Raman scattering. The rest of the experimental setup was the same as the SERS.

Since some energy is absorbed by the sample solution, a small fraction of the scattered light will have a different frequency, μ_i , and ΔE corresponds to this absorbed energy as :

$$\Delta E = h [\mu_o - \mu_i] \quad (4.1)$$

The frequency, μ_o , may be in any region of the spectrum but the difference, $[\mu_o - \mu_i]$ is of the magnitude of an infrared (vibrational) frequency. Raman Scattering is the process which produces light of frequency other than μ_o . In the case of Raman Scattering radiation with $\mu_i < \mu_o$, it is known as Stokes radiation while anti-Stokes radiation represents $\mu_i > \mu_o$. The differences, $[\mu_o - \mu_i]$ is measured in Raman spectroscopy. Also, the scattered light can be either polarized parallel or perpendicular before entering the double monochromator. The Normal Raman spectra for a 0.1N MTAB solution is shown in Figure 4.4. The assignments of the peaks are :

TABLE 4.1 Assignments of Normal Raman for MTAB	
wavenumber(cm^{-1})	assignment
2846	CH_2 symmetric stretch
2885	CH_2 asymmetric stretch
2925	CH_2 symmetric stretch
2960	CH_2 overtone of scissoring

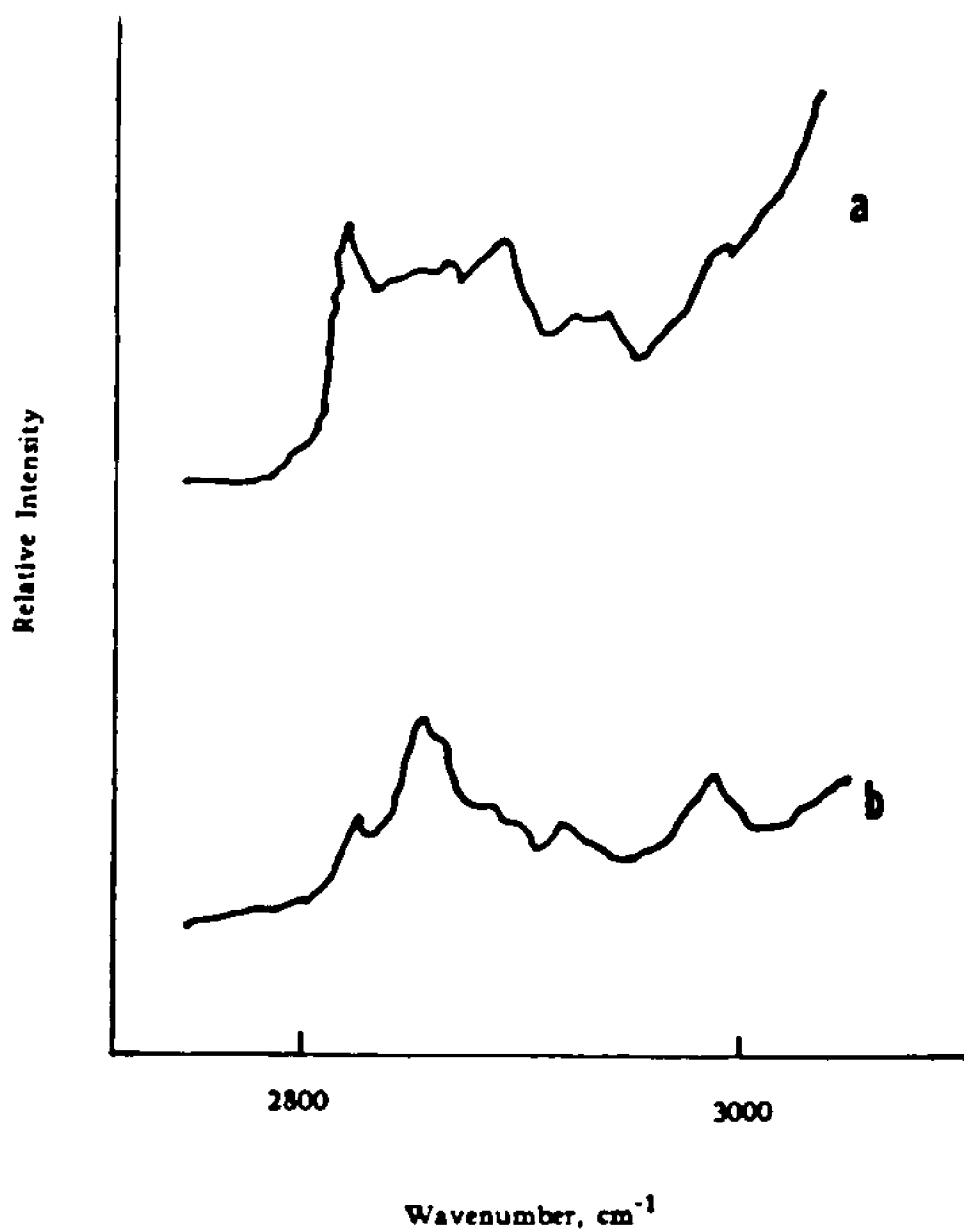


Figure 4.4 Normal Raman Scattering spectra of 0.1N Myristyltrimethylammonium Bromide
a) parallel polarization b) perpendicular polarization

All the four peaks are either from the CH_2 stretches or scissoring modes, or in other words, from the hydrocarbon tail of the surfactants. These peaks from the Normal Raman can be used to identify the surfactant for the SERS experiment.

4.5. SURFACE ENHANCED RAMAN SCATTERING SPECTROSCOPY

After the silver electrode was polished mechanically with the alumina slurry, the electrode was pretreated in 0.1N KCl solution using a double potential step of -0.30V to 0.30V versus SEC and then returning to -0.30V. The spectra for 0.01N MIAB in 0.05N KBr solution were shown in Figure 4.5. It is a three-dimensional plot of frequency, applied potential and relative intensity as the x-y-z coordinate respectively. Those four peaks obtained which belong to the hydrocarbon tail of the surfactant are identical to the ones from Normal Raman. At low negative potentials, the intensity of the peaks are low. As the potential decreases, the increase in intensity indicates two phenomena. The first, more cationic surfactant is adsorbed at the more negative surface, resulting in an increase of intensity of the peaks. The second, in order to make room for more adsorption, the orientation of the surfactant may change from flat to a vertical position. Moreover, it has to be in a head-on position so that the hydrocarbon tail is free from the surface in order for such an increase in intensity to occur. At extreme potentials, the decrease in intensity is due to production of hydrogen ions at the electrode, which is discharging ions and is over the limit of polarization already.

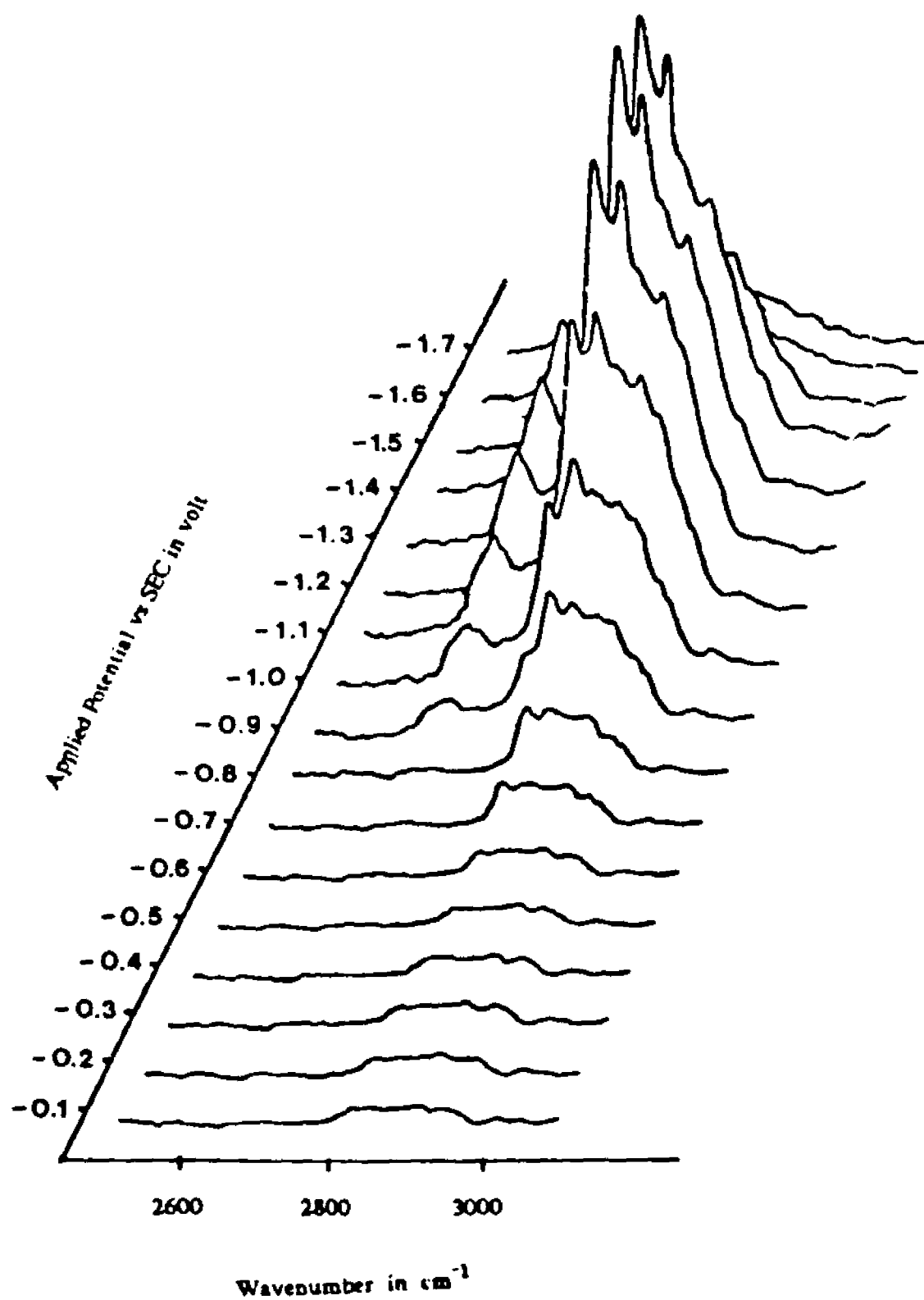


Figure 4.5 Surface Enhanced Raman Scattering spectra of Myristyltrimethylammonium Bromide

4.6. DISCUSSION

From the electrocapillary experiment, it is found that amphoteric and anionic surfactant adsorbed at moderate and anodic potentials respectively. However, for cationic surfactants, as the potential is decreased beyond the point of zero charge, the interfacial pressure drops gradually back to zero. It seems that adsorption only takes place at moderate potentials. This phenomenon can have two different possible explanations :

- i) Supporting electrolyte ions give strong competition with the cationic surfactant, and at high negative potential, they may displace the surfactant from the mercury surface. However, desorption of cationic surfactant from the negative charged mercury surface seems improbable.
- ii) The cationic surfactant is so strongly adsorbed at the mercury surface that the polar head group of the surfactant is losing its lateral repulsion. Interfacial pressure arises mostly from the repulsion of the charged head groups or the dipole-dipole interaction for ionic surfactants. If there is a decrease in lateral repulsion, that will result in decrease of interfacial pressure.

From Figure 3.19 for MTAB, the adsorption isotherms indicate the formation of condensed liquid film at the anodic branch. When the mercury is negatively charged, solid film of cationic surfactant is formed. This shows that the second explanation is the more probable one. Furthermore, from the SERS result, there is proof that there is more adsorption of cationic surfactant at a more negative surface. This also suggests that the correct explanation for the electrocapillary experiment is that cationic surfactant is so strongly adsorbed at the negative charged mercury surface that the polar head group is losing the lateral repulsion, resulting in a decrease in pressure. The interaction between the surfactant and the surface is so strong that the surfactant forms a solid or condensed liquid film around the mercury drop. This explanation could also be supported by

monolayer experiments (10). When a fatty acid was spread on water, surface pressure increased if the surface was compressed. However, if a trace of calcium ions was added, a condensed liquid film formed and there was no increase in surface pressure when compressed.

The results of both electrocapillary and SERS experiments show that cationic surfactant interacts more strongly with a negative charged surface than an anionic or amphoteric surfactants with a charged surface. Also, the orientation of the adsorbed surfactant on a highly charged surface is a perpendicular head-on position which produces dewetting.

4.7. CONCLUSION

It was found that fluorocarbon oil containing surfactant(s) can dewet solid surfaces. In order to achieve dewetting, the surfactant must be adsorbed in a head-on position with the hydrocarbon tail facing outward. This will change the solid surface from hydrophilic to hydrophobic. Water will then be separated from the fluorocarbon oil simply by the density difference. This method will produce a dry, spotless, and clean surface which is particularly important in the electronic industry.

From dewetting tests, it was shown that electrostatic forces play an important role in the adsorption of the surfactant. The ion-ion interactions are high enough to keep the surfactants in the fluorocarbon solvent from being extracted into the water phase (in most cases). With the polar head of the surfactant adsorbed onto the charged solid/liquid interface, solid will emerges dry from the fluorocarbon surfactant solution. In order to investigate the electrostatic effects, electrocapillary experiments were performed. It was found that amphoteric and anionic surfactants adsorbed at moderate and anodic potential respectively. Cationic surfactant appeared to be only adsorbed at moderate potential as the

interfacial pressure decreases back to zero in the anodic branch. Usual interpretation of this behaviour of electrocapillary curves is desorption. Further study of cationic surfactants, however, indicated the formation of solid films at negatively charged mercury surface.

Surface Enhanced Raman Scattering technique was used to further investigate the adsorption of the cationic surfactant at solid/liquid interface. It was proved that at high negative potential, there is more adsorption of the cationic surfactant and the surfactant is adsorbed in a head-on position which will produce dewetting. It was then concluded that cationic surfactants interact strongly with the negatively charged solid surface. When the surface is more negatively charged, the closer the cationic surfactant will be adsorbed on the surface and the less the lateral repulsion of the polar head group will be. A solid type of film is formed at the solid/liquid interface and it is this layer of surfactant responsible for dewetting.

Since the interaction of the cationic surfactant and the charged solid surface is stronger than the ones for the anionic and amphoteric surfactants, this explains why cationic surfactant solution was able to dewet glass (high negatively charge surface) spontaneously while anionic and amphoteric surfactants required several immersions before dewetting could be achieved.

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APPENDIX

The numerical method used is the Modified Regula Falsi to solve for the roots of a complicated function. Usual successive substitution method does not work since the absolute value of the derivative of the function is less than one in the region of interest. Following is a listing of the program in Fortran 77 using the VAX system.

PROGRAM LISTING

```

      external z
      common/znt/nt,t,potential,gamma1
      real*8 z,a,b,w,gamma1
c     do 7 i=1
5    continue
      dtol=1e-8
      ftol=1e-8
      ntol=50
      nt=0
      a=10.0
      b=800.0
      call mrg(z,a,b,dtol,ftol,ntol,w,lfag,n)
      if(t.le.0.0)stop      write(6,600)potential,gamma1
600 format(1x,f13.6,4x,f13.6)      goto 5
      end
c
c
c
      double precision function z(gamma)
      common/znt/nt,t,potential,gamma1
      real*8      l,r,gamma,h,u,dhgd,g,alpha,k,n,rad,beta,s,hb,pi,gamma1
      gamma1=gamma
      if (nt .ne. 0) goto 20
      write (0,90)
90    format ('Type value of potential and drop time')
      read(5,*)potential,t
      nt=1
20    continue
c

```

```

c
c
c
c   This is the equations used for converting drop
c   time into interfacial tension.
c
c
c   l = length of the capillary tube in cm
c   r = radius of the capillary tube in cm
c   t = drop time in second
c   gamma = interfacial tension in dynes/cm
c   h = applied hydrostatic cpressure in cm of mercury
c   dhg= density of mercury in g/cc
c   d = density of electrolyte solution in g/cc
c   u = viscosity of mercury in poise (g/cm/s)
c   g = gravity in cm/s**2
c   alpha = buoyancy factor
c   k = poiseuille's formula
c   m = mass is gram in air of detached drop
c   rad =radius of curvature of the mercury drop
c   Beta= Harkin's correction factor due to incomplete detachment
c   s = a term in Smith's equation
c   hb = Smith's correction for back pressure
c
c
c   pi=3.1415928
c   l=15.2
c   r=2.2778e-3
c   u=0.015289
c   dhg=13.534
c   d=0.99707
c   g=980.0
c   alpha=(dhg-d)/dhg
c   k=(pi*(r**4.0)*(dhg**2.0)*g)/(8.0*u*l)
c   m=(2.0*pi*r*gamma)/(alpha*g)
c   beta=3.680*r/(m**(1.0/3.0))
c   rad=(3.0*m/(4.0*pi*dhg))**(1.0/3.0)
c   s=3.0*gamma/(rad*dhg*g)
c   h=70.94+1.59*alpha
c   hb=s+s**2.0/(3.0*h)
c
c
c   Equation for the dropping mercury
c
c   z=2.0*pi*r*gamma-alpha*g*k*(1.0+beta)*(h-hb)*t
c
c
c   return
c   end
c
c
c
c

```

```

c
c
c
c
c      subroutine   mrg(f,a,b,dtol,ftol,ntol,w,lfag,n)
c      ****
c      f is the function f(x) whose zero is to be found.
c      Name must be in the external statement in the calling program.
c      a,b are the end points of the interval wherein zero is sought.
c      dtol is the desired length of the output interval.
c      ftol is the desired size of f(w).
c      ntol is the maximum number of iteration steps that
c           will be carried out.
c
c
c      ****
c      w is the best estimate of the zero found
c
c      lfag an integer, and
c          = -1 as failure as f(a) and f(b) has same sign
c          = 0  termination as abs(a-b) .le. dtol
c          = 1  termination as abs(f(w)) .le. ftol
c          = 2  termination as ntol iteration steps were carried out
c
c
c      **** *method* ****
c      the method used is modified regula falsi method
c      at each iteration, linear interpolation between the points
c      (a,fa) and (b,fb) is used.
c
c      given that f(x) is continuous on (a<b) and f(a)*f(b).le.0
c      set f=f(a),g=f(b) w0=a
c      for n=0,1,2,3,4,-----until satisfied, do
c      calculate wn+1=(g*an-f*bn)/(g-f)
c      if f(an)*f(wn+1).le.0, set
c          an+1=an,bn+1=wn+1,g=f(wn+1)
c      if also f(wn)*f(wn+1).gt.0 set f=f/2
c      otherwise,set an+1=wn+1,bn+1=bn,f=f(wn+1)
c      if also f(wn)*f(wn+1).gt.0 set g=g/2
c      then f(x) has a zero in the interval (an+1,bn+1)
c      ****
c      external f      common/znt/nt,t,potential,gamma1
c      real*8 f,a,b,w,fa,fb,fw,gamma1
c      fa=f(a)          if(t.le.0.0)return
c      signfa=dsign(1.d0,fa)
c      fb=f(b)
c      lfag=-1
c
c      w=a
c      fw=fa
c      do 20 n=1,ntol
c      if(dabs(a-b).le.dtol)then
c      lfag=0

```

```

    return
  end if
c
  if(dabs(fw).le.ftol)then
    lfag=1
    return
  end if
c
  w=(fa*b-fb*a)/(fa-fb)
  prvsfw=dsign(1.d0,fw)
  fw=f(w)
  if(signfa*fw.gt.0)then
    a=w
    fa=fw
    if(fw*prvsfw.gt.0.) fb=fb/2.
  else
    b=w
    fb=fw
    if(fw*prvsfw.gt.0.) fa=fa/2.
  end if
20 continue
  lfag=2
  return
end

```

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