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THE EFFECT OF INTERFACIAL PHENOMENA ON MASS
TRANSFER RATES IN LIQUID - LIQUID SYSTEMS

Ph.D. Thesis

University of London

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September 1963

The following is a corrected version of the Table headings on
pages 172 and 186:

Runs 143 - 153 ... Transfer of Phenol from Water to Benzene Drop

In addition, on page 119, line 2, for "increasing" substitute "decreasing".

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Thesis
presented for the
Degree of Doctor of Philosophy, University of London

by

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ABSTRACT

Qualitative investigations have shown that mass transfer in liquid-liquid systems takes place in three different regimes. These have been termed diffusional, eruptive and turbulent, with the type of transfer depending on the "driving Force" and the magnitude of surface pressure gradients set up by local surface renewal at the interface. The present work concerns itself with the experimental procedures and quantitative aspects of the physical quantities in the three regimes inasmuch as it shows the influence of interfacial phenomena on the rate of mass transfer.

The quantitative determinations of mass transfer coefficients were carried out using an apparatus designed for drop formation and withdrawal, special arrangements enabling the drop volume and time of formation to be kept constant. A "viscous traction" surface viscometer was employed for the determination of surface viscosity and is described in detail.

Results are given for the system benzene-acetic acid-water with the direction of transfer from the benzene to the aqueous continuous phase, and for the system benzene-phenol-water for the transfer in both directions. They indicate that surface viscosity and the group $\Delta\pi/\eta_{si}$ do not critically affect the rate of mass transfer and that the important variable is the "surface strain" (given by the ratio of change in surface pressure to the surface compressional modulus) i.e. the strain to which the interface is subjected by eddies and movements from within the bulk phase. A certain value of this "surface strain" must exist before the mass transfer rate will increase.

In the diffusional regime the experimental mass transfer coefficients were in fair agreement with those calculated theoretically on the basis of the penetration theory. In the eruptive and turbulent regimes a correlation is given between the ratio of the mass transfer coefficient to its value in the diffusional regime and the change in surface pressure, evaluated on the basis of a new model.

The addition of soluble surface active agents to the aqueous phase has a pronounced effect on the mass transfer rate, decreasing

it by as much as 75% for only a minute trace of surface active agent. The effect of the surface active agent is purely hydrodynamical in nature and it presents no direct barrier to mass transfer at the interface. The results show that whereas surface viscosity is relatively unimportant, surface compressibility is an extremely important variable in interphase transfer.

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1. INTRODUCTION

A large number of separation processes employed in the chemical industry rely on the transfer of a substance from one phase into another. Thus, knowledge of the rate at which this inter-phase mass transfer occurs is of great importance, particularly in the design of separation equipment. The commonly accepted mechanisms proposed for its prediction assume that the transfer takes place by molecular diffusion, either through thin stagnant films adhering to the interface or into elements of fluid which are periodically replaced at the interface by the turbulent motion of the bulk fluid. Also, it is assumed that the interface does not interfere with the transfer process in any way.

It has been felt for a long time, particularly as a result of difficulties in correlating mass transfer data in liquid-liquid extraction, that this theoretical model does not adequately represent the conditions existing in inter-phase mass transfer. This made necessary a closer look at the transfer process.

The basic equation for the calculation of mass transfer rates in liquid-liquid extraction is

$$N' = K_{od} (C_d - C_{di}) \quad \dots \quad 1.1$$

where the symbols are as indicated below. The overall mass transfer coefficient is obtained as

$$1/K_{od} = 1/k_d + m/k_c \quad \dots \quad 1.2$$

and the individual coefficients are given by correlations of the type

$$Sh_d = \alpha Re_d^p Re_c^q Sc_d^{r'} \quad \dots \quad 1.3$$

$$Sh_c = \beta Re_c^{s'} Re_d^{t'} Sc_c^u \quad \dots \quad 1.4$$

where N is the mass flux, K_o the overall mass transfer coefficient, C the concentration of solute in the bulk phase, C_i the concentration of solute at the interface in the same phase, k the individual film coefficient, m the distribution coefficient, Sh the Sherwood number, Re the Reynolds number and Sc the Schmidt number; c denotes the continuous phase, d the dispersed phase and p, q, r', s', t', α and β are constants.

The above relationships and procedural methods for determining mass transfer rates were, however, found to be of restricted validity, particularly in liquid-liquid extraction. Usually they were applicable only to the particular system and particular equipment for which the values of the constants were established. Any attempts to produce a more generalised correlation were fruitless, thus indicating that the above equations were insufficient or incomplete to define the process.

According to equations 1.3 and 1.4 the mass transfer coefficient in a given phase is represented as a function of the hydrodynamic behaviour of the bulk of the two phases (characterised by Re_c and Re_d) and by the molecular transport characteristics of the phase through which the transfer takes place (Sc and D in the Sherwood number). The resistances to mass transfer are then added, assuming that the interface does not interfere with the transport process in any

way. However, there are cases in which the latter assumption may not be justified.

The interface is not a geometric plane; it possesses a small but finite thickness and there are forces existing in it which are different from those in the bulk phases. Therefore, the interface ought to be regarded as a separate and distinct phase. Should the transport process interfere in any way with the equilibrium of forces existing there, movements in the interface could result, affecting the value of the mass transfer coefficient and the hydrodynamic behaviour close to the interface so that the latter would no longer be fully described by the bulk Reynolds number.

Consider a pair of immiscible solvents with solute S being transferred from solvent A to solvent B (Fig. 1.1a). The solute S is positively adsorbed at the interface, i.e. an increase in concentration decreases the interfacial tension (Fig. 1.1b). The concentration of solute in solvent A at the interface is C_{Ai} and σ_i is the interfacial tension corresponding to this concentration.

Let us now assume that an eddy brings to the surface material of bulk concentration C_{Ab} . This will produce a local reduction of interfacial tension by $\Delta\sigma$ and disturb the equilibrium of forces at the interface. Since the interfacial tension difference can be regarded as stress acting in a plane, a gradient of interfacial tension will cause motion in the interface (Marangoni effect¹) until equilibrium is

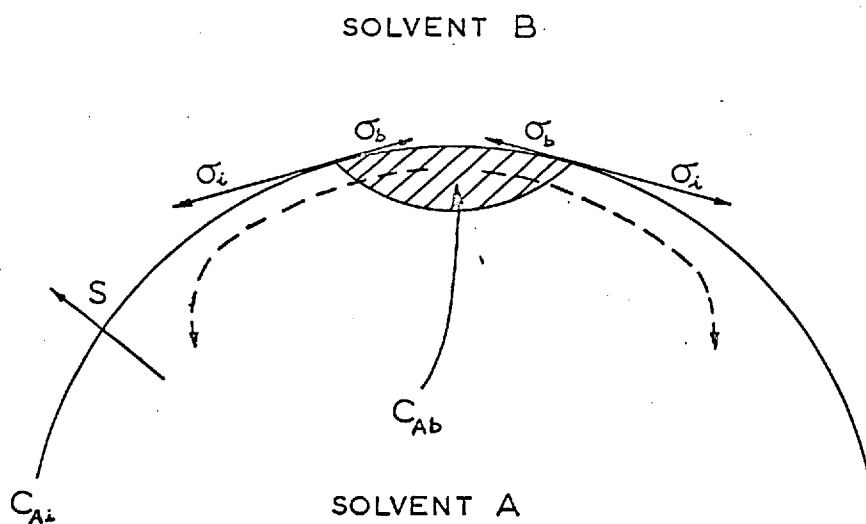


FIG. 1.1a

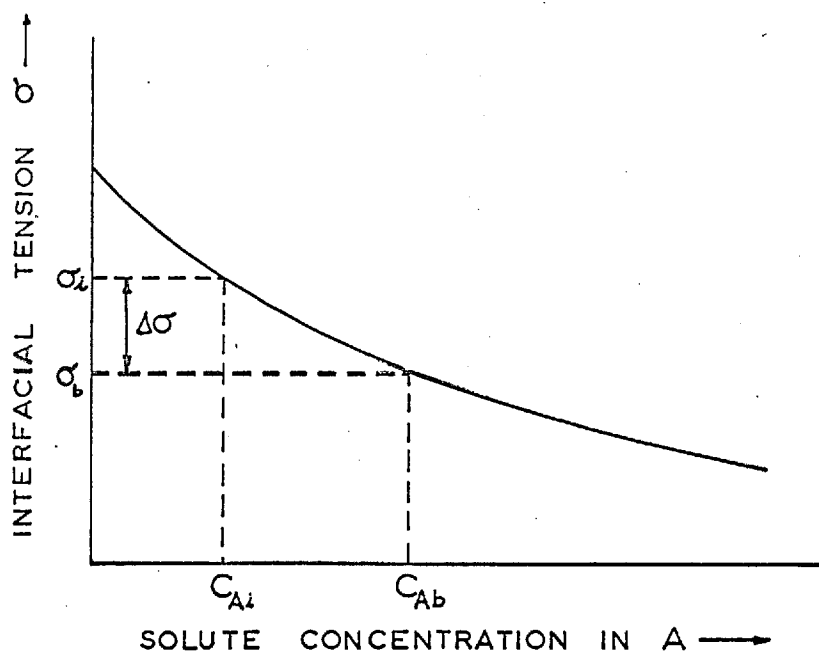


FIG. 1.1b

restored. This motion exerts a drag on the adjoining sublayers, thus increasing the rate of surface renewal and the value of the mass transfer coefficient. It may also affect the interfacial area, by causing a contraction of films flowing down a column or accelerating or decelerating the coalescence of droplets.

The present work is concerned with the influence of interfacial phenomena on the values of mass transfer coefficients. A qualitative study of existing phenomena and some preliminary determinations of mass transfer rates was made by Goltz²; this work has been improved upon and extended to include mass transfer in the presence of surface active agents and the effects of some interfacial parameters.

2. LITERATURE SURVEY

2.1 Theories of Mass Transfer

The theory most frequently applied to liquid-liquid systems is Whitman's³ two-film theory for gas absorption. Here it is assumed that stagnant films of negligible capacity exist on either side of the interface and that these films offer all the resistance to mass transfer. Any turbulence disappears near the interface or free surface and the flow is thus considered to be laminar and parallel to the surface. For convenience it is assumed that this film can be regarded as a layer of thickness z and the mechanism is one of diffusion through this layer, the rate of transfer for dilute solutions being given by

$$N' = \frac{D}{z} (C - C_i) \quad \dots \quad 2.1$$

where

- N' is the mass flux
- z is the thickness of the stagnant film
- C is the concentration of solute in the bulk phase from which the transfer takes place
- C_i is the concentration of solute at the interface based on the same phase
- D is the diffusivity

Since z is generally not known, D/z is replaced by k , a mass transfer coefficient for each film. Hence the mass flux through both films, N , is given by

$$N' = k_d (C_d - C_{di}) \quad \dots \quad 2.2$$

$$N' = k_c (C_{ci} - C_c) \quad \dots \quad 2.3$$

where d and c denote the two phases respectively.

Since the concentration at the interface is frequently not known an overall mass transfer coefficient K_o , based on the known overall driving force, is defined by the equation

$$N' = K_{od} (C_d - mC_c) \quad \dots \quad 2.4$$

$$= K_{oc} (C_d/m - C_c) \quad \dots \quad 2.5$$

where m is the distribution coefficient, defined by

$$m = C_{di}/C_{ci} \quad \dots \quad 2.6$$

From equations 2.2 - 2.6 it can be shown that the individual film and overall mass transfer coefficients are related by the equation

$$1/K_{od} = 1/k_d + m/k_c = m/K_{oc} \quad \dots \quad 2.7$$

While the film theory has been useful in giving a physical picture of the process and in comparing mass transfer rates in a given piece of equipment and for a given system under different operating conditions, it has not led to a universally satisfactory method of predicting mass transfer coefficients. The assumption of steady state diffusion is rarely true in practice, for the surface is continuously being renewed with fresh liquid from the bulk of the solution - brought by eddies to the interface. Thus at a given moment the surface of the liquid is a mosaic of elements of different "ages", with the rate of transfer varying according to age. The average rate of transfer depends on the distribution of the elements of the surface among the various "age groups".

This is taken into account by the penetration theory, which

considers mass transfer as unsteady state diffusion into a semi-infinite medium. This theory requires the solution of the partial differential equation for diffusion

$$\frac{\partial C}{\partial t} = D_d \frac{\partial^2 C}{\partial z^2} \quad \dots \quad 2.8$$

Using suitable boundary conditions this equation can be solved to give

C as a function of time and distance from the interface

$$C = C_d + (C_{di} - C_d) \operatorname{erfc} (z/2\sqrt{D_d t}) \quad \dots \quad 2.9$$

The instantaneous mass flux N' is given by

$$N' = -D_d \left[\frac{\partial C}{\partial z} \right]_{z=0} \quad \dots \quad 2.10$$

Therefore, from equations 2.9 and 2.10

$$N' = \sqrt{D_d/\pi t} (C_d - C_{di}) \quad \dots \quad 2.11$$

where t is the age of the interface, i.e. its time of contact with the other phase. The mean mass flux $\bar{N}'$ is obtained from the expression

$$\bar{N}' = \int_0^\infty \phi(t) N' dt \quad \dots \quad 2.12$$

where $\phi(t)$ is the surface age distribution function, that is to say the fraction of the surface having ages between t and $(t + dt)$. The form of this distribution function must be known or postulated.

Higbie⁴ postulated a simple solution in which each element of surface is exposed for the same length of time θ before being replaced, i.e. regular surface renewal. Thus

$$\left. \begin{aligned} \phi(t) &= 1/\theta \quad \text{for } 0 \leq t \leq \theta \\ \phi(t) &= 0 \quad \text{for } t > \theta \end{aligned} \right\} \quad \dots \quad 2.13$$

$$\text{then} \quad \bar{N}' = 2\sqrt{D_d/\pi\theta} (C_d - C_{di}) \quad \dots \quad 2.14$$

Danckwerts⁵ suggested a probably more realistic model for films flowing over randomly arranged packings and stirred liquids. He postulated that there is no correlation between the age of an element of surface and its chance of being replaced. In other words, all elements have at any time equal probabilities of being replaced. Thus

$$\phi = s e^{-st} \quad \dots \quad 2.15$$

where s is the fractional rate of surface renewal, and

$$\bar{N}' = \sqrt{D_d s} (C_d - C_{di}) \quad \dots \quad 2.16$$

Although this theory gives what is probably a truer picture of the actual conditions prevailing in practice, by allowing for renewal of an interface by turbulence, it has since been shown by Toor and Marchello⁶ that the film and penetration theories are not mutually exclusive, but form two limiting cases of a more general theory known as the film-penetration theory. Here, the fluid particles - which are continuously exchanged by turbulence - are considered not as semi-infinite layers but as being of finite depth $z = L$, say. Using suitable initial and final boundary conditions the solutions obtained

$$\text{are} \quad \bar{N}' = \sqrt{D_d s} \left[1 + 2 \sum_{n=1}^{\infty} \exp(-2nL\sqrt{s/D_d}) \right] (C_d - C_{di}) \quad \dots \quad 2.17$$

$$\text{or} \quad \bar{N}' = \sqrt{D_d s} \left[1/L(D_d/s)^{\frac{1}{2}} + L/3(s/D_d)^{\frac{1}{2}} - L^3/45(s/D_d)^{\frac{3}{2}} \dots \right] (C_d - C_{di}) \quad \dots \quad 2.18$$

For intensive surface renewal (large s) equation 2.17 reduces, approximately, to 2.16, and for small s 2.18 reduces to 2.1.

2.2 Interfacial Phenomena

During the past decade a number of ternary systems have been discovered experimentally in which the interface was found to be disturbed during mass transfer by eruptions and spasms, whilst the nearby regions were agitated spontaneously. This phenomenon, known as interfacial turbulence, has more than academic importance since it is invariably accompanied by mass transfer rates which may be several times higher than the theoretical ones predicted by the two-film theory^{7,8,9,10,11,12,13,14}.

Ward and Brooks¹⁵ were the first to report the existence of spontaneous, highly localised, interfacial agitation accompanying mass transfer although, about the same time, Lewis and Pratt¹⁶ observed the spontaneous oscillation of droplets when they were attempting to measure non-equilibrium interfacial tensions by the pendant drop method. Battacharya¹⁷, studying mass transfer across moving interfaces, observed spontaneous movements in the interface. Since then interfacial turbulence has been studied in drops and flat interfaces, both visually and photographically.

Thus, Kroepelin and Neumann¹⁸ photographed convective streams within pendant droplets. These convection currents emanated from the end of the capillary and flowed through the drop as a jet. On reaching the interface this jet caused a deformation of the droplet and an eruption was initiated at the interface. Thus, turbulent mixing was produced in the droplet interior and further supply from the capillary

produced a new eruption. In a further paper¹⁹ they have shown that for eruptions to occur the equilibrium of forces existing at the interface must be disturbed, that is to say adjacent areas of the surface must have different interfacial tensions and this gives rise to violent tangential movements at the interface. The same authors²⁰ have photographed the flat turbulent interface of the system ethyl acetate-acetic acid-water in profile, using a schlieren apparatus, and have shown that eruptive mass transfer can take place across plane interfaces, and that interfacial activity is assisted by density gradients in the direction of transfer.

Kroepelin and Prött^{21,22} have shown that interfacial turbulence may also be produced when mass transfer takes place across a gas-liquid interface. Interference pictures²³ showed the disturbance created at the surface when methanol vapour was allowed to contact the surface of water. The disturbance was produced by local absorption of methanol creating points of different interfacial tension, causing rapid movement in the direction of the areas of higher interfacial tension.

Spontaneous emulsification and ejection of droplets has been reported by Kroepelin and Neumann^{24,25} who also explained these phenomena in terms of interfacial tension changes. Sherwood and Wei¹¹, whilst studying mass transfer with interfacial chemical reaction, noticed the occurrence of spontaneous turbulence in the phase boundary regions and they found that interfacial turbulence was pronounced in the case of exothermic neutralizations.

Pendant droplets disturbed by rippling, pulsation, kicking and eruptions were studied by Lewis and Pratt¹⁶, Haydon²⁶ and Garner et al²⁷. Haydon²⁸ also investigated the kicking of pendant drops both qualitatively and quantitatively and proposed a mechanism for it. Sigwart and Nassenstein^{29,30} made an extensive photographic study of eruptions in pendant drops using a colour schlieren technique. They showed that the eruptions were caused by changes in interfacial tension, which in turn were produced by concentration changes, usually by convective currents. In many systems they observed eruptions irrespective of the direction of transfer. In particular, the interfacial activity of the system carbon tetrachloride-acetic acid-water was photographed cinematographically in colour by Nassenstein and Kraus³¹. The schlieren technique has also been used by Kroepelin and Neumann¹⁸ and Goltz³² to photograph the kicking, oscillation and rotation of pendant drops. Several investigators have found that rising and falling drops behave in the same manner as pendant ones^{30,33,34}

Almost all of the above-mentioned experimental observations indicated that the phenomenon of interfacial turbulence, as the name implies, is a chaotic and disorganised process. However, some semblance of ordered flows was shown to be possible by directing a thin jet of solute toward a flat interface between two immiscible liquids^{19,30}. More recently Linde^{35,36,37} and Orell & Westwater³⁸ have succeeded in showing that spontaneous interfacial flows can occur in a cellular pattern. This spontaneous interfacial cellular convection accompanying mass transfer has been studied photographically using a schlieren technique.

Many investigators agree that interfacial motion is triggered by local variation of interfacial tension, namely the Marangoni effect^{18,19,26,30,32}. Yet until recently there was in existence only the limited theory of interfacial turbulence in drops advanced by Davies and Haydon³⁹. In 1959 Sternling and Scriven⁴⁰ put forward a theoretical quantitative mechanism for the onset of interfacial turbulence operating in a flat interface. They considered interfacial turbulence to be a manifestation of hydrodynamic instability. Their theory maintains that small ever-present fluctuations of concentration or temperature about the interface may, under favourable conditions, be spontaneously amplified into fully developed flows, by the Marangoni effect. Such flows may be either highly irregular ones - corresponding to interfacial turbulence - or ordered flows that presumably arrange themselves in a regular cellular pattern which one may term "cellular convection". The basic unit of flow is a roll cell within which liquid is circulating. The roll cells are presumed to be analogous to Benard cells for heat transfer, which are exhibited by an unconfined horizontal thin layer of pure liquid heated from below. Sternling and Scriven found interfacial turbulence to be promoted by steep concentration gradients near the interface, by systems exhibiting a large rate of change of interfacial tension with solute concentration and by the absence of surface active agents as well as large differences in kinematic viscosity and diffusivity in the two phases. They have also shown that for positively adsorbed solutes the interface is unstable for mass transfer out of the phase of higher viscosity and lower diffusivity.

2.3 Effect of Surface Active Agents.

The effect of surface active agents on mass transfer rates in liquid-liquid extraction has been studied extensively by several workers^{27,34,42,43,44,45,46,47,48,49,50,51,52}. All the investigations have shown that the presence of a surface active agent causes a marked decrease in the mass transfer rate. The various explanations advanced as to the nature of the additional resistance to mass transfer caused by the presence of the surface active agent can be classified either as barrier theories or as hydrodynamic theories. The former category is based on the assumption that surface active molecules adsorbed at a liquid-liquid interface form a kind of barrier which interferes with the passage of diffusing solute molecules, whereas the latter presupposes that the adsorbed molecules are somehow capable of modifying the hydrodynamic conditions in the vicinity of the interface. Earlier workers^{45,48,51,52} have favoured the barrier theory, but the results of more recent work by Boye-Christensen and Terjesen^{41,42} and by Gordon and Sherwood⁵³ favour the hydrodynamic theory. Very recently Thorsen and Terjesen⁵⁴ have confirmed the findings of the latter workers and have also proposed a hydrodynamic theory based on interfacial turbulence with boundary layer separation for the case of drops falling through an aqueous continuous phase.

Until very recently no quantitative experimental work on the influence of interfacial phenomena on mass transfer rates in liquid-liquid extraction has been published. Sawistowski and Goltz⁵⁵ have since shown that there exist two distinct regimes of mass transfer;

these are called the diffusional and the turbulent regimes and they are separated by a transitional regime. In the diffusional regime the experimentally determined mass transfer coefficients were in reasonably good agreement with those calculated on the basis of the penetration theory. Mass transfer coefficients in the turbulent regime depended on the local increase in interfacial tension and on the concentration level of the solute in the droplet phase.

The present work is a continuation of this latter investigation in an attempt to provide more information on the influence of interfacial phenomena on mass transfer rates in liquid-liquid extraction. Part of the investigation covered by this thesis has already been published⁵⁶ and a reprint of the paper is submitted at the back of this binding.

3. TYPES OF TRANSFER

Qualitative investigations have shown that there exist three distinct regimes of mass transfer, which have been termed diffusional, eruptive and turbulent.

The diffusional regime is characterised by a smooth droplet surface surrounded by a diffusional layer, which is removed by free convection. It is usually associated with low driving forces and with the presence of surface active agents, or impurities. A schlieren photograph of this phenomenon is shown in Plate 3.1 Acetic acid is being transferred from a benzene drop to the surrounding aqueous continuous phase. The concentration of acetic acid in the benzene drop is 0.15 M and in the aqueous phase 0.00 M. The photograph illustrates the diffusional layer, shown as a dark border to half the drop, and as a lighter border to the other half. The light portion in the centre of the drop is due to the lens effect of it, and represents the image of the pinhole which is out of focus.

The eruptive regime is characterised by a tangential pulling away of the diffusional layer, followed usually by a normal ejection of solute into the bulk of the continuous phase - hence the term eruptive. The eruptions usually occur at moderate driving forces and are often repeated periodically, but with quite a large deviation of the period from the mean. Plates 3.2(a) to 3.2(d) show schlieren photographs of an eruption in progress, at different time intervals. The example is again that of acetic acid transferring from a benzene drop to aqueous continuous phase.

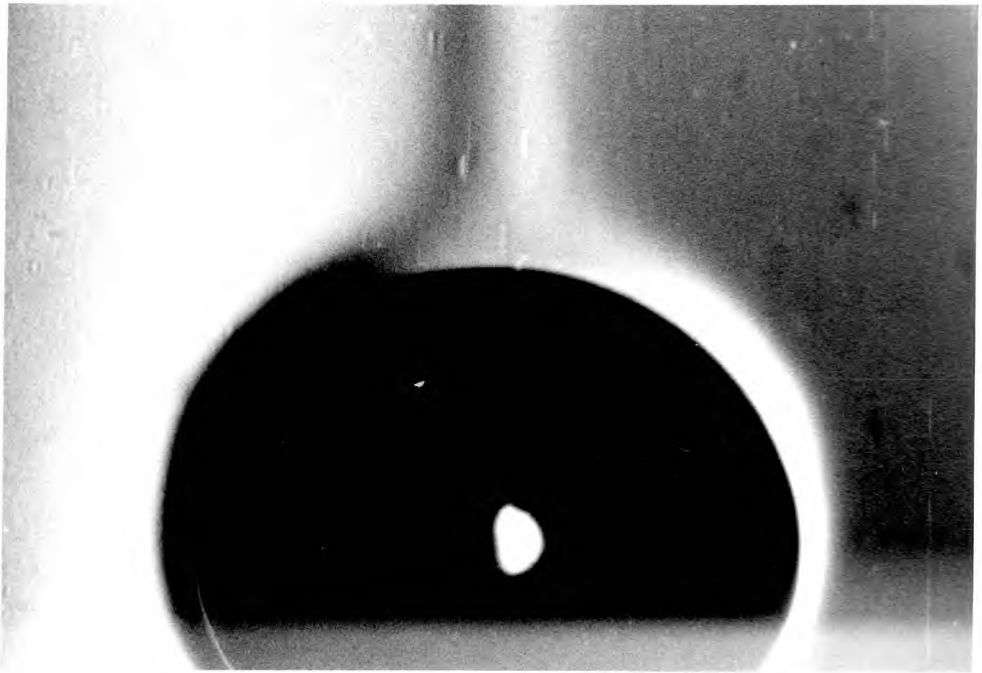
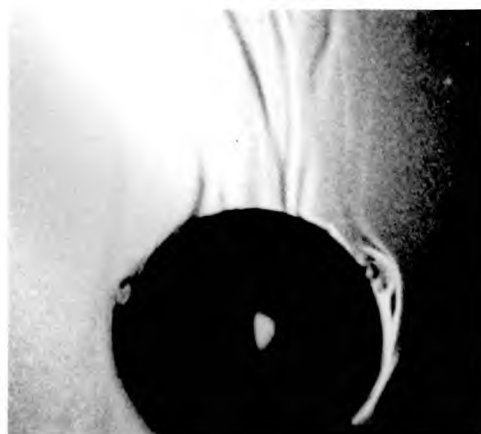


PLATE 3.1 : DIFFUSIONAL REGIME



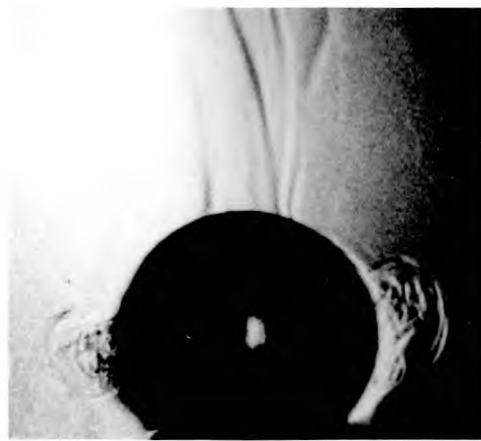
(a) 0 secs.



(b) 0.047 secs.



(c) 0.094 secs.



(d) 0.156 secs.

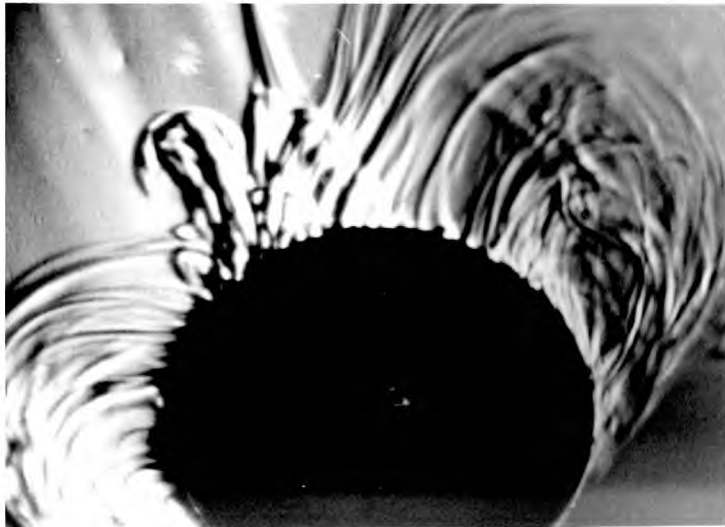
PLATE 3.2 : ERUPTIVE REGIME

Initially, in Plate 3.2(a), the droplet has a smooth surface surrounded by the diffusional layer; the remaining three photographs show the same droplet 0.047, 0.094 and 0.156 seconds later respectively. The diffusional layer can be seen to be completely destroyed. Subsequently, it is rapidly reformed and the process repeats itself. The mechanism of an eruption is described at the end of this chapter.

In the turbulent regime the number of eruptions has increased to such an extent that one can hardly speak of individual eruptions. Instead, the whole of the droplet surface is in a continual state of strong turbulence. This regime is associated with large driving forces. Plates 3.3(a) and 3.3(b) show schlieren photographs of this regime for the transfer of acetic acid from the benzene drop to the aqueous continuous phase (concentration of acetic acid in benzene phase 2.0 M, concentration of acetic acid in aqueous phase 0.0 M), and Plate 3.4 shows the transfer of phenol from aqueous continuous phase to the benzene drop (concentration of phenol in aqueous phase 1.0 M, concentration of phenol in benzene phase 0.0 M). In the latter example the dark and light areas around the droplet surface correspond to sudden decreases in phenol concentration in the aqueous phase at the interface. Phenol was found to be far more surface active in character than acetic acid, and although the above regimes were observed for the transfer of phenol from a benzene drop to the aqueous continuous phase, the values of the driving force at which the transition from one regime to another occurred differed appreciably.



(a)



(b)



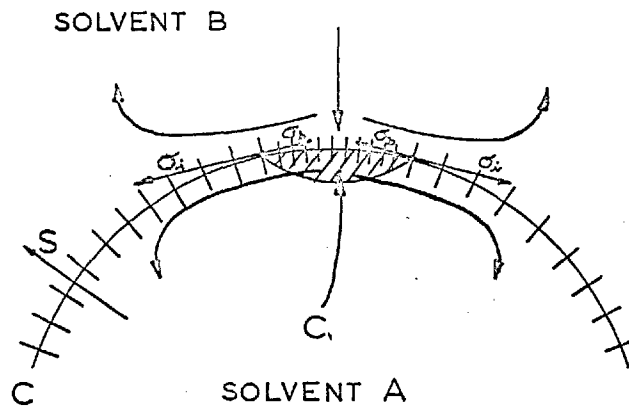
PLATE 3.4 : TURBULENT REGIME

Mechanism of an Eruption

Consider a pair of immiscible solvents A and B , with solute S being transferred from solvent A to solvent B (Fig. 3.1(a)). Solute S is positively adsorbed at the interface, that is to say an increase in concentration causes a decrease in interfacial tension (Fig. 3.1(b)) and the concentration of solute at the interface is C_{Ai} giving an interfacial tension σ_i .

Let us now assume that an eddy brings material of bulk concentration C_{Ab} to a small area of the surface (shown shaded in Fig. 3.5(a)). This area, being the more concentrated in solute S , will have a lower interfacial tension σ_b than its surroundings, and hence an interfacial tension gradient is set up. This local reduction of interfacial tension $\Delta\sigma (= \sigma_i - \sigma_b)$ (Fig. 3.1(b)) will disturb the equilibrium of forces existing in the interface and produces a rapid outward tangential movement of the interface and of the adjoining sublayers (Fig. 3.1(a)). Thus, the two phases are brought into direct contact and a high rate of mass transfer results. However, this outward tangential movement produces a compression of the adsorbed molecules, giving new points of low interfacial tension at C and D (Fig. 3.1(c)). A centripetal motion follows, resulting in a throwing out of the transferred solute S into the bulk of the solvent B (Fig. 3.1(c)). This mechanism explains the motion perpendicular to the interface that is frequently associated with eruptions.

Using a high-speed cine camera, the interface of the benzene-acetic acid-water system has been photographed at speeds up to 3,000 frames



SOLVENT A

FIG. 3.1a

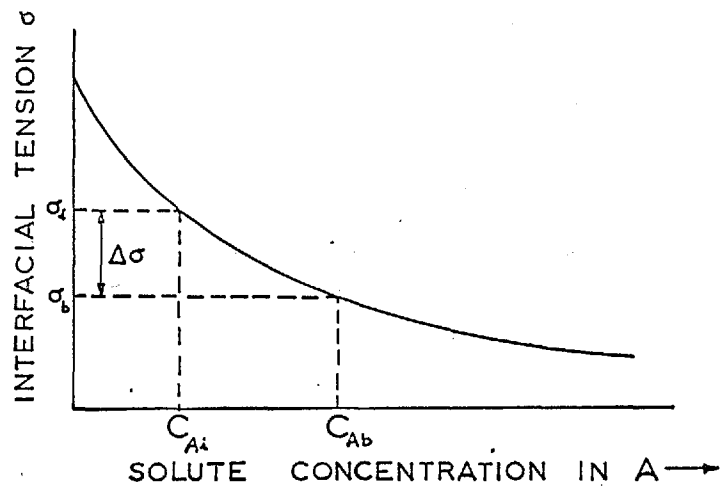
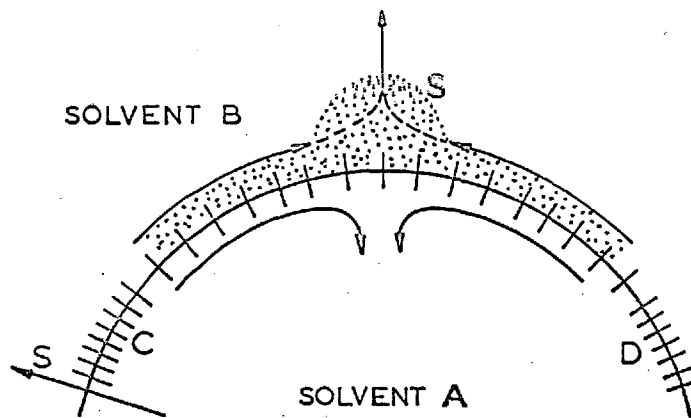


FIG. 3.1b



SOLVENT A

FIG. 3.1c

MECHANISM OF AN ERUPTION

frames per second. Observations of the interface during an eruption confirmed the movements in the interface explained above and presented further proof for the eruptive mechanism.

4. THE SCHLIEREN SYSTEM

A schlieren arrangement was used in all investigations to enable visual observation of the interface. Hence a direct comparison could be made between the mass transfer coefficient obtained and the behaviour of the interface during the mass transfer process.

The basis of the schlieren system, described in detail by Schradin⁵⁷, is the deviation of some of the rays of light owing to changes in refractive index, which in turn may be brought about by changes in concentration and temperature.

The schlieren system used in the investigations is shown diagrammatically in Fig. 4.1. It consists of a 250 watt high pressure mercury vapour lamp as the source of light S. The beam of light was then focused on a pinhole P by means of the lens L_1 ; the pinhole could now be considered as a point source of light. The distance PL_1 was equal to the focal length of the lens L_2 . The schlieren object was placed between the lenses L_2 and L_3 . The beam of light from the lens L_3 was focused on a knife edge K, i.e. L_3K is the focal length of the lens L_3 , and the image of the object was focused on a screen I or on a photographic plate or film. Changes in concentration in the cell (due to mass transfer) give rise to refractive index changes and consequently a deviation of the light will result. The light will be deflected on to or off the knife edge, correspondingly producing dark or light regions on the screen.

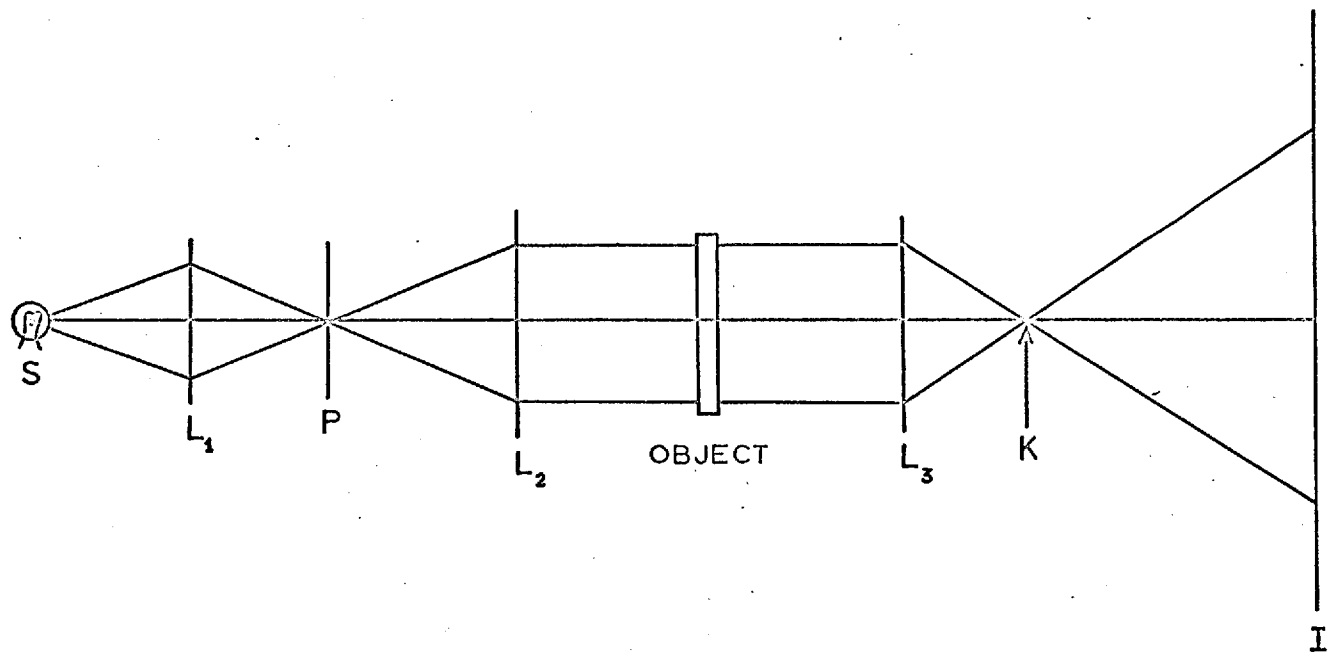


FIG. 4.1: THE SCHLIEREN SYSTEM

5. EXPERIMENTAL TECHNIQUE AND APPARATUS

The experimental techniques employed in the present work are modifications of techniques used in previous work on liquid-liquid extraction in the Department of Chemical Engineering, Imperial College of Science and Technology, London.

The main problem in the quantitative work was to reduce the number of variables to a minimum. Since the critical drop size, i.e. that at which the drop would detach from the nozzle, is a function of the interfacial tension, a method had to be developed for working below the critical drop size and producing drops whose size would be independent of interfacial tension. The method finally adopted consisted of drop formation and withdrawal (a technique first used by Skinner⁵⁸ and later by Goltz²) and the apparatus and procedure is described in detail below.

The basis of the drop formation and withdrawal apparatus is shown schematically in Fig. 5.1. Two DCL micropumps with diaphragm heads and fitted with 1/8" plungers were used to form and withdraw the drops. The stroke of the pumps could be adjusted during operation by means of a micrometer screw. This adjustment was so arranged that the drops did not reach their critical size (that is to say the size at which they would detach from the nozzle) and therefore the drop size was independent of the physical properties of the systems studied. Both pumps were driven by a governor-controlled variable-speed motor so that at any instant the two plungers of the pumps were in the same

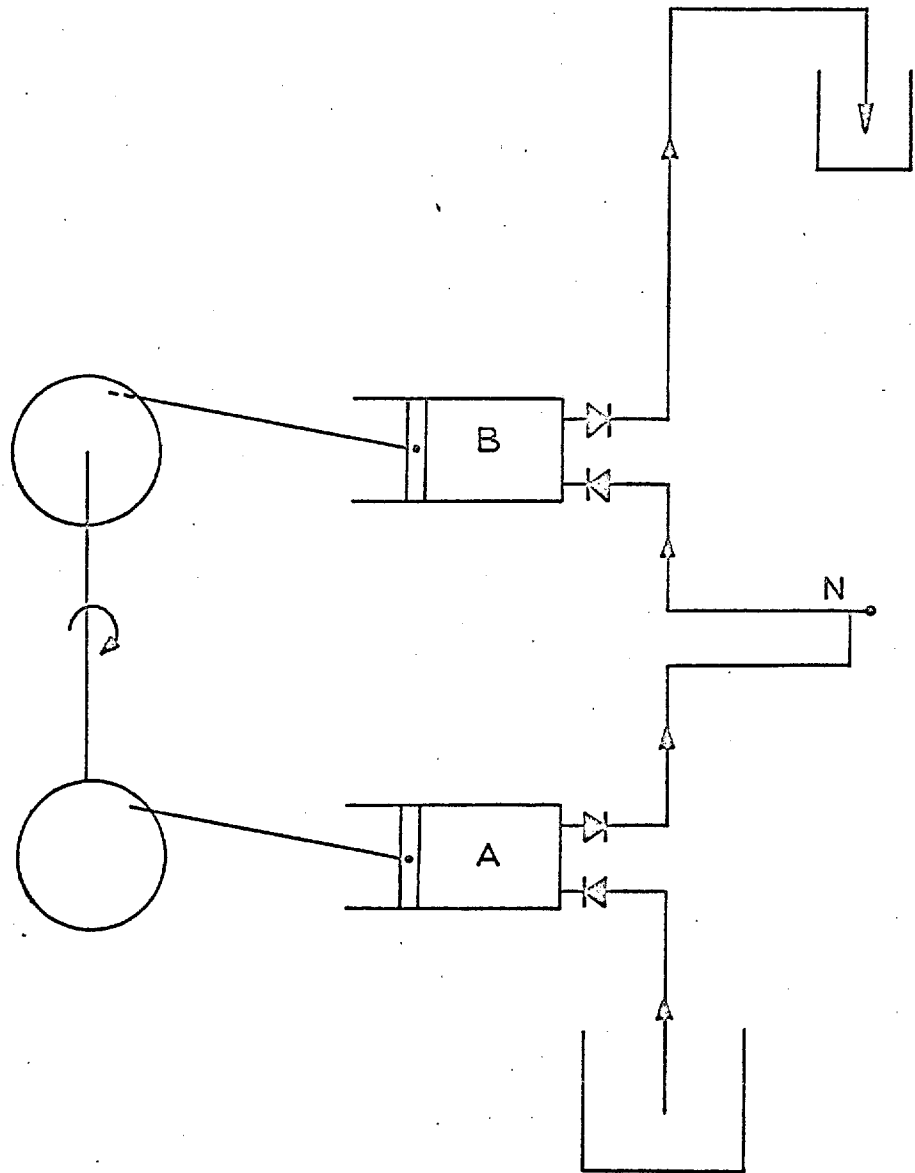


FIG. 5.1: SCHEMATIC DIAGRAM OF DROP FORMATION AND WITHDRAWAL APPARATUS

relative position. By adjustment of the motor speed the time of formation of the drops could be maintained constant.

Pump A will draw fresh solution from the reservoir while pump B withdraws the drop from the end of the nozzle N. During the delivery stroke pump A will form a drop at N, while pump B will discharge the withdrawn solution. Thus, at no time will the droplet remain stationary on the end of the nozzle.

The volumetric discharge of pump A was measured at each integral micrometer position from 0 to 7, and the resulting calibration curve is shown in Fig. 5.2 For all experiments the micrometer setting of pump A was 2.00, while that of pump B was adjusted so that the interface of the withdrawn drop always returned to the same position.

Fig. 5.3 shows the relation between the ratio of the time of drop formation to the time taken for the pump to complete one revolution and the pump micrometer position. This ratio was obtained from the angle through which the pump moved before striking the stops. From the graph it can be seen that for the pump micrometer position of 2.00 this ratio is 0.173. This means that only 0.346 of the cycle is spent in forming and withdrawing the drop; the remaining 0.654 of the cycle pertains to the condition when the drop is withdrawn and will be called the stagnant period.

Fig. 5.4 shows the increase in drop volume with time up to

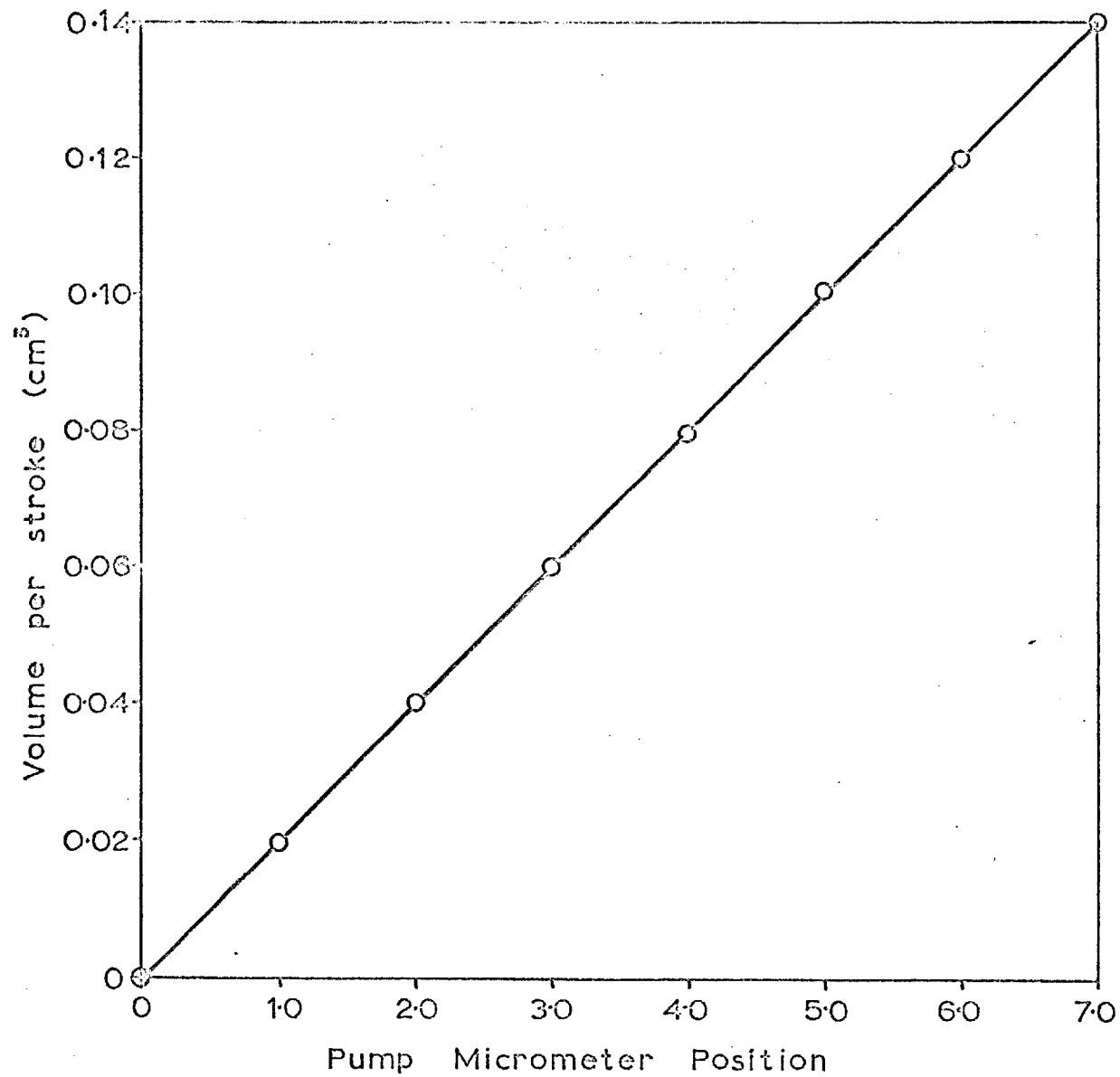


FIG. 5.2: PUMP CALIBRATION No. 3 - 887.

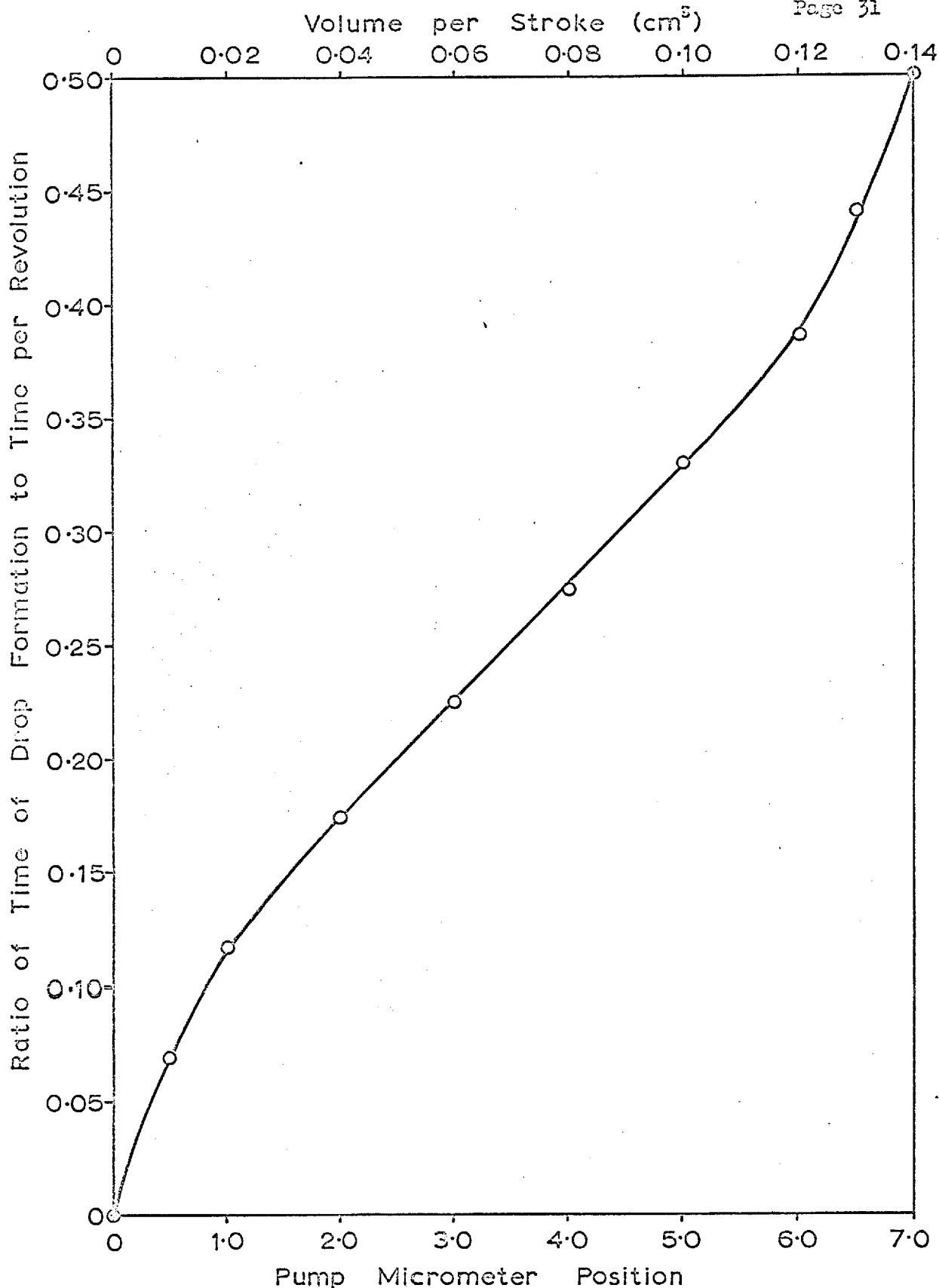


FIG.5.3:RELATION BETWEEN THE RATIO OF THE TIME OF DROP FORMATION TO THE TIME TAKEN FOR ONE COMPLETE PUMP REVOLUTION AND THE PUMP MICROMETER POSITION

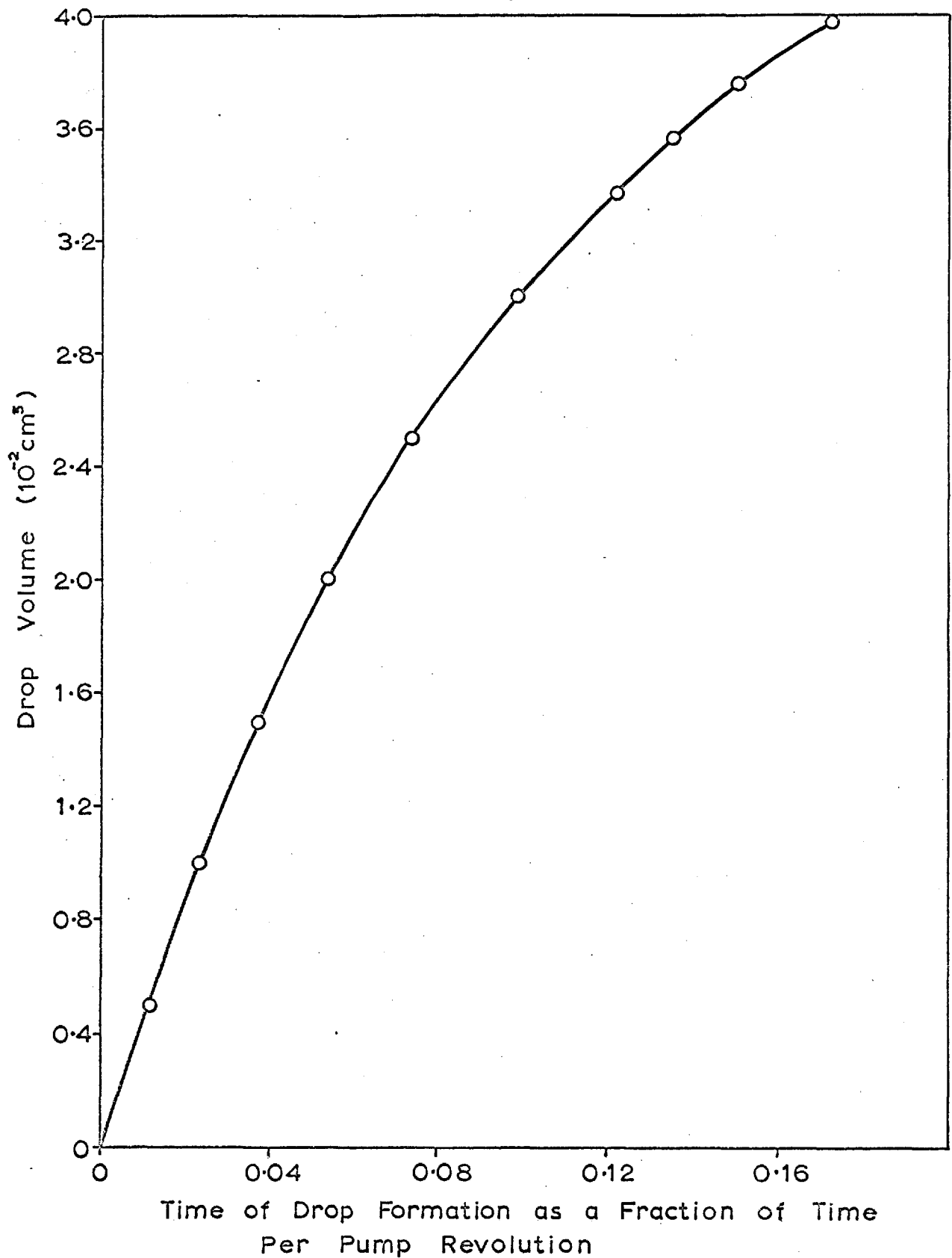


FIG. 5.4: THE VOLUME-TIME RELATIONSHIP (pump position 2.0)

0.173 of the time of one complete revolution for a micrometer setting of 2.00. During the drop formation stroke the plunger will move from the position indicated by the micrometer position 2.00, time ratio 0.173, to the origin on Fig. 5.3

In order to calculate the free interfacial area of the drop it has been assumed that the exposed portion is always a section of a perfect sphere, the centre of which is moving out along the axis of the nozzle. From a knowledge of the diameter of the tip of the nozzle a relation between the free interfacial area and the drop volume was calculated. Using the data of Fig. 5.4 the dependence of the free interfacial area (for pump micrometer position 2.00) on time, as a fraction of the time of the complete revolution, can be derived, and this is shown in Fig. 5.5. The value at the beginning of the stroke represents the area of the tip of the nozzle of diameter 0.267 cm. From this curve, the time mean area per cycle was calculated and found to be 0.1612 sq. cm.

Figs. 5.6 and 5.7 show details of the nozzle. It consisted of a glass capillary tube fitted with a capillary side arm. The nozzle tip was an accurately machined stainless steel "cap" which was fixed to the glass capillary tube with Araldite. The outside of the tip was machined at 45° to the axis so that a sharp edged tip was formed with the bore. A thin stainless steel tube was introduced through the tip so that its free end was about 1.5 mm above the plane of the top and inside the nozzle. This tube was then sealed with

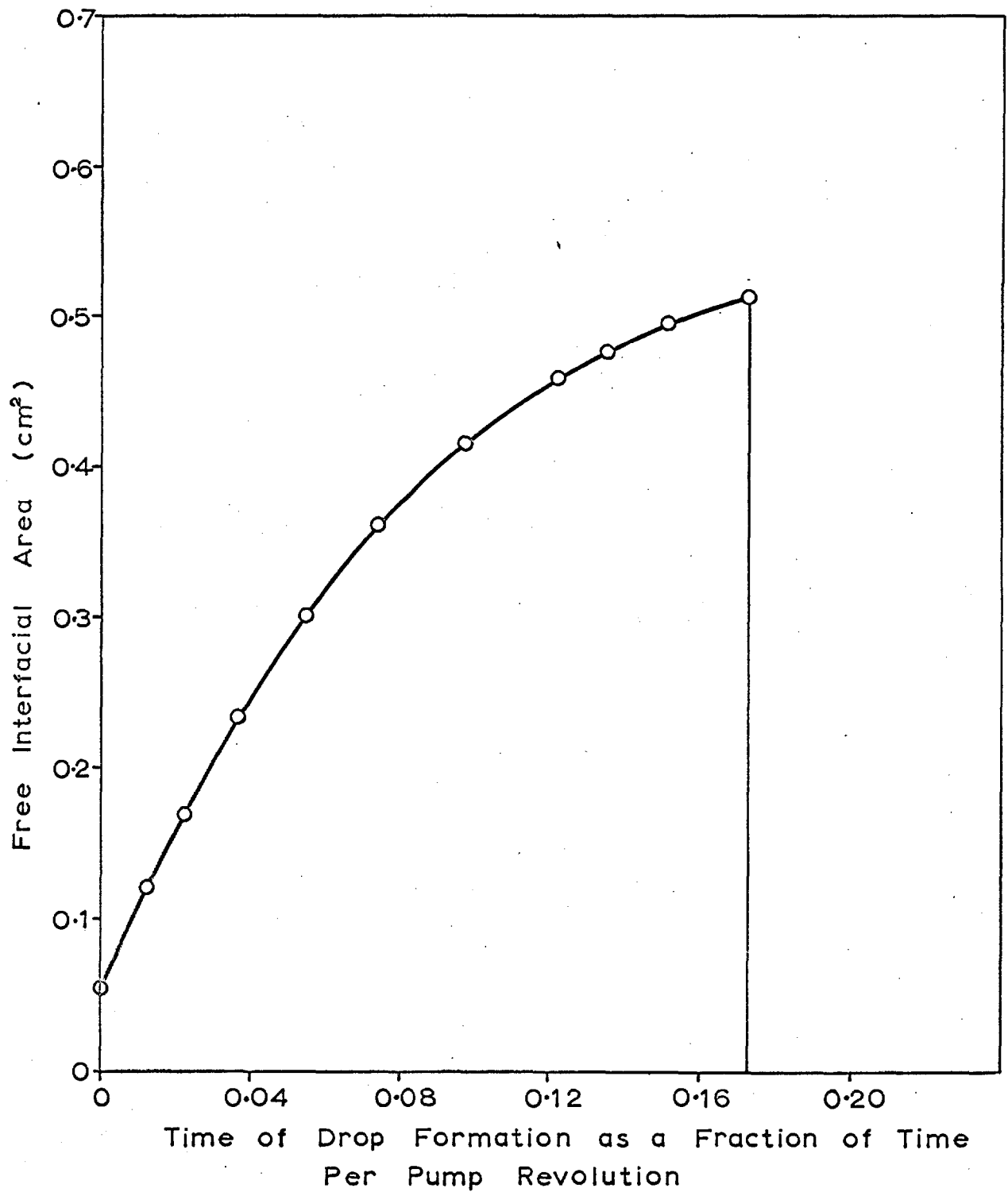


FIG. 5.5: THE FREE AREA - TIME RELATIONSHIP

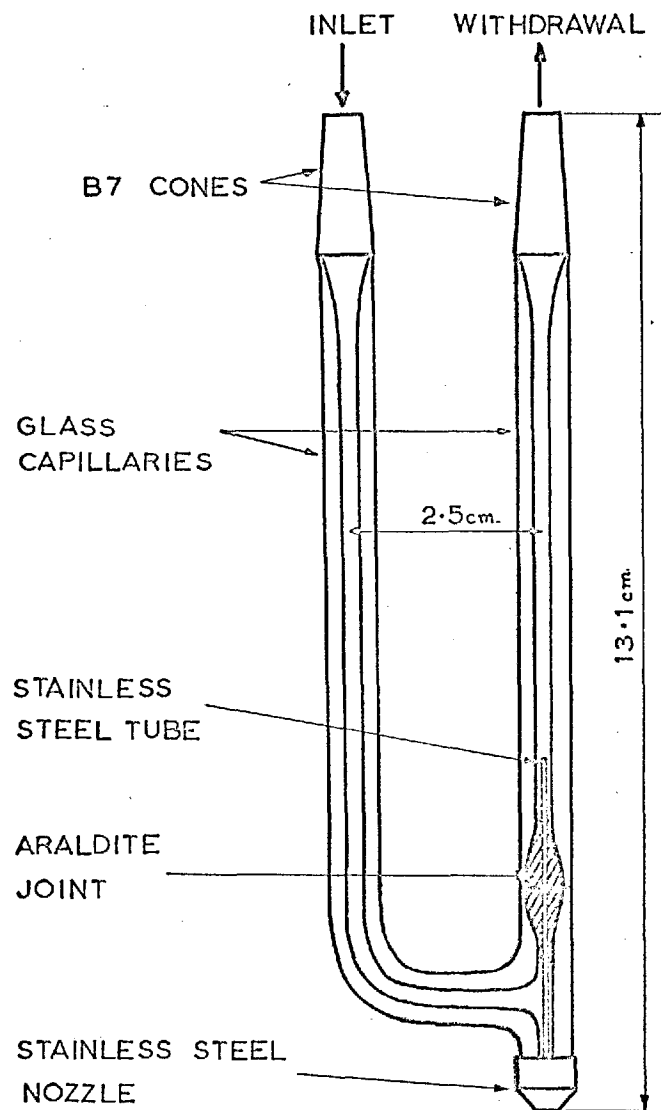


FIG. 5.6

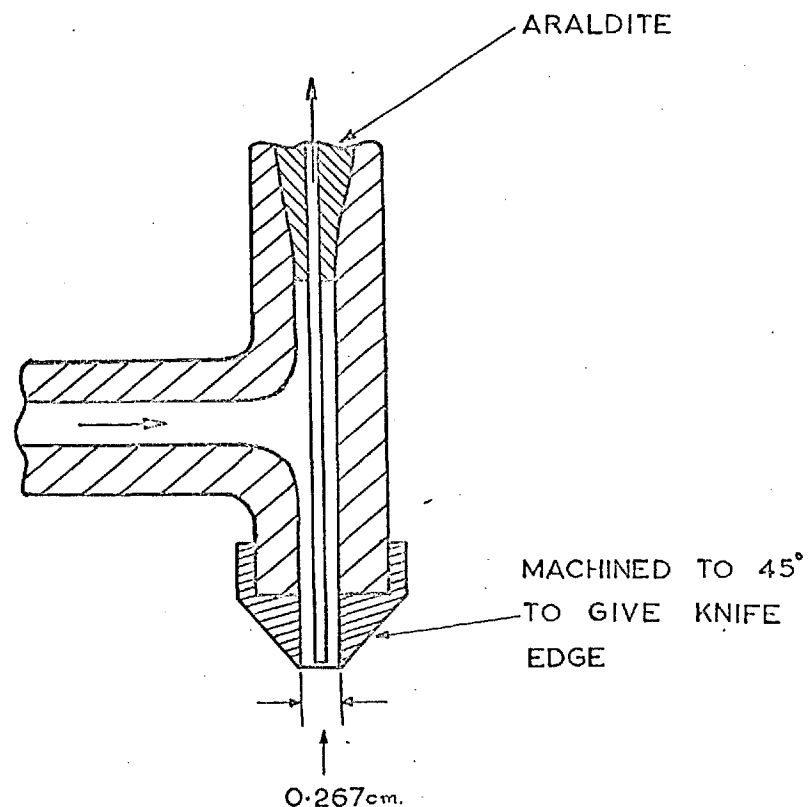


FIG. 5.7

DETAILS OF NOZZLE

Araldite in the withdrawal arm of the nozzle above the entrance of the capillary sidearm. Hence pump A forms the drop through the annulus and pump B withdraws the drop through the stainless steel tube.

With the exception of the stainless steel pumps, the nozzle cap and the joints from the pumps to the glass tubing (which were made of rigid polythene, previously soaked in benzene for a long time), the apparatus was made of glass, with hemispherical joints where accurate alignment was impracticable. The diagrammatic arrangement is shown in Fig. 5.8; Plate 5.1 is a photograph of the apparatus.

The vertical outlet tube from the discharge pump B had to be long in order to provide sufficient head of liquid to cause the valves to seal. A sample point was located near the bottom of this tube in order to reduce the time lag between drop withdrawal and sampling, as well as to avoid evaporation, which would occur at the top or after liquid had passed through the overflow tube.

During each run the nozzle set-up was placed in a stainless steel cell fitted with parallel plate glass windows; the continuous phase flowed through this cell entering at the bottom and leaving by an overflow tube, as shown in Plate 5.2. The cell was placed in the schlieren field to allow for direct comparison of experimental results with visual observation, i.e. a correlation between measured transfer rates and the type of transfer.

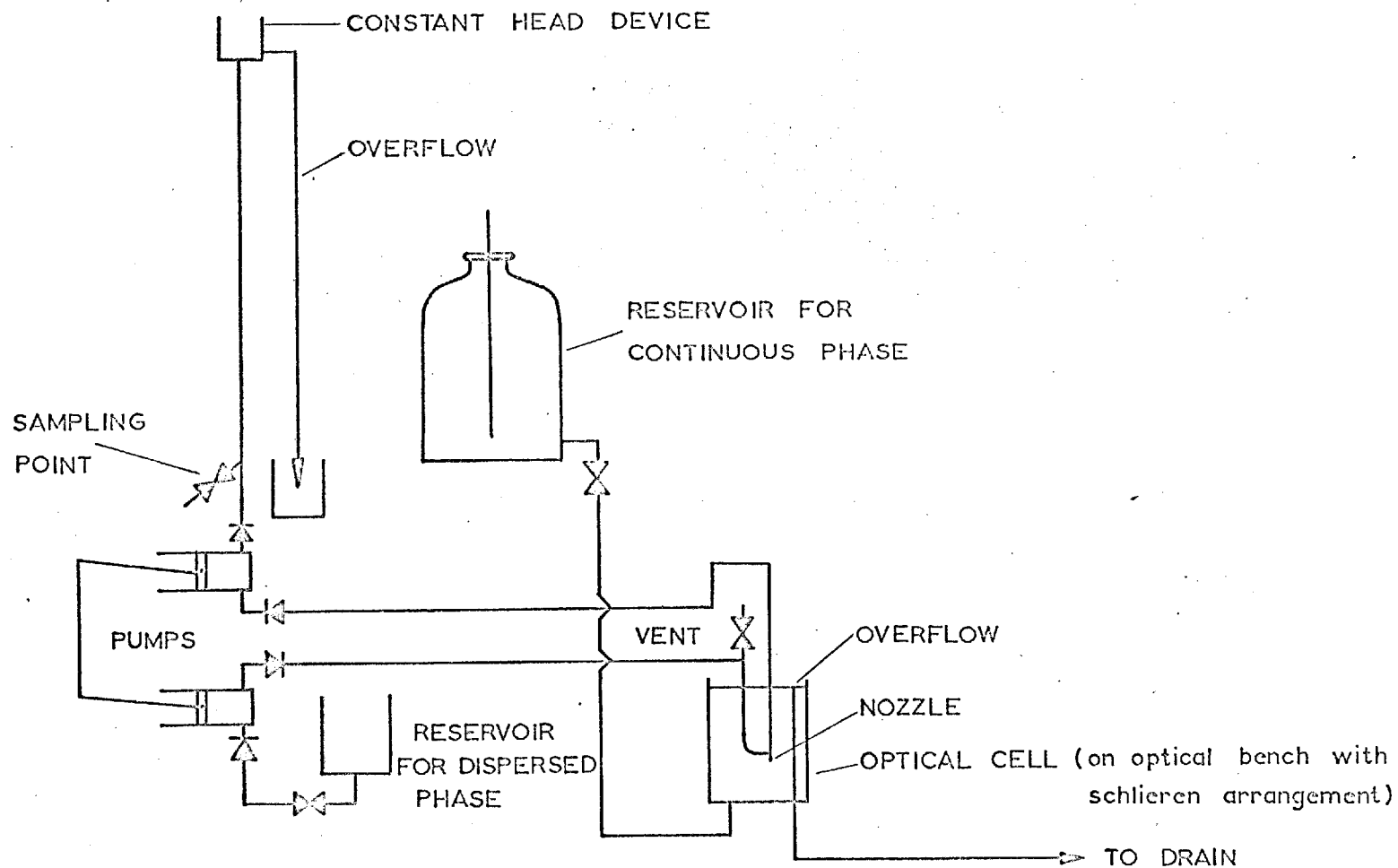


FIG.5.8: DIAGRAMMATIC ARRANGEMENT OF APPARATUS

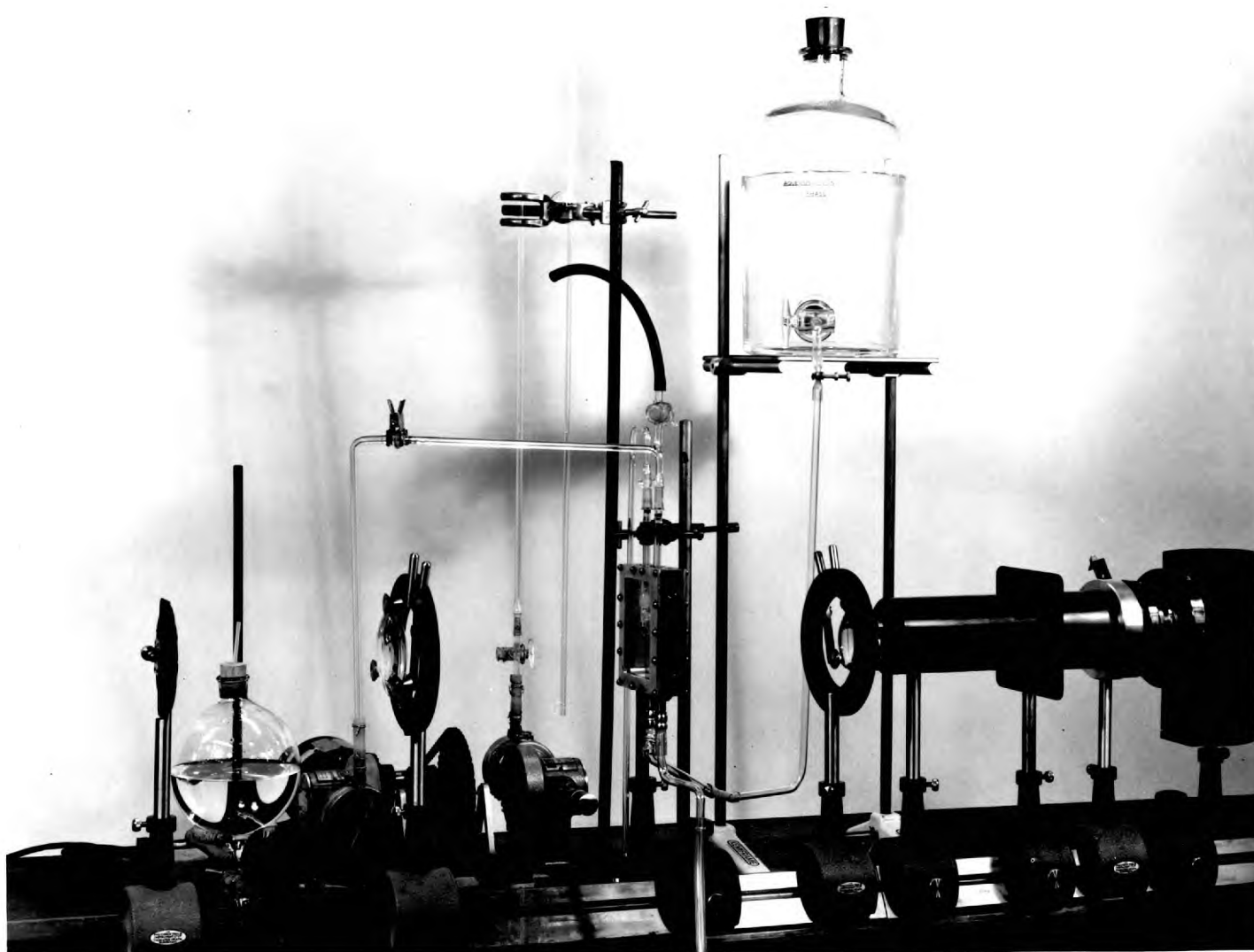


PLATE 5.1 : PHOTOGRAPH OF APPARATUS

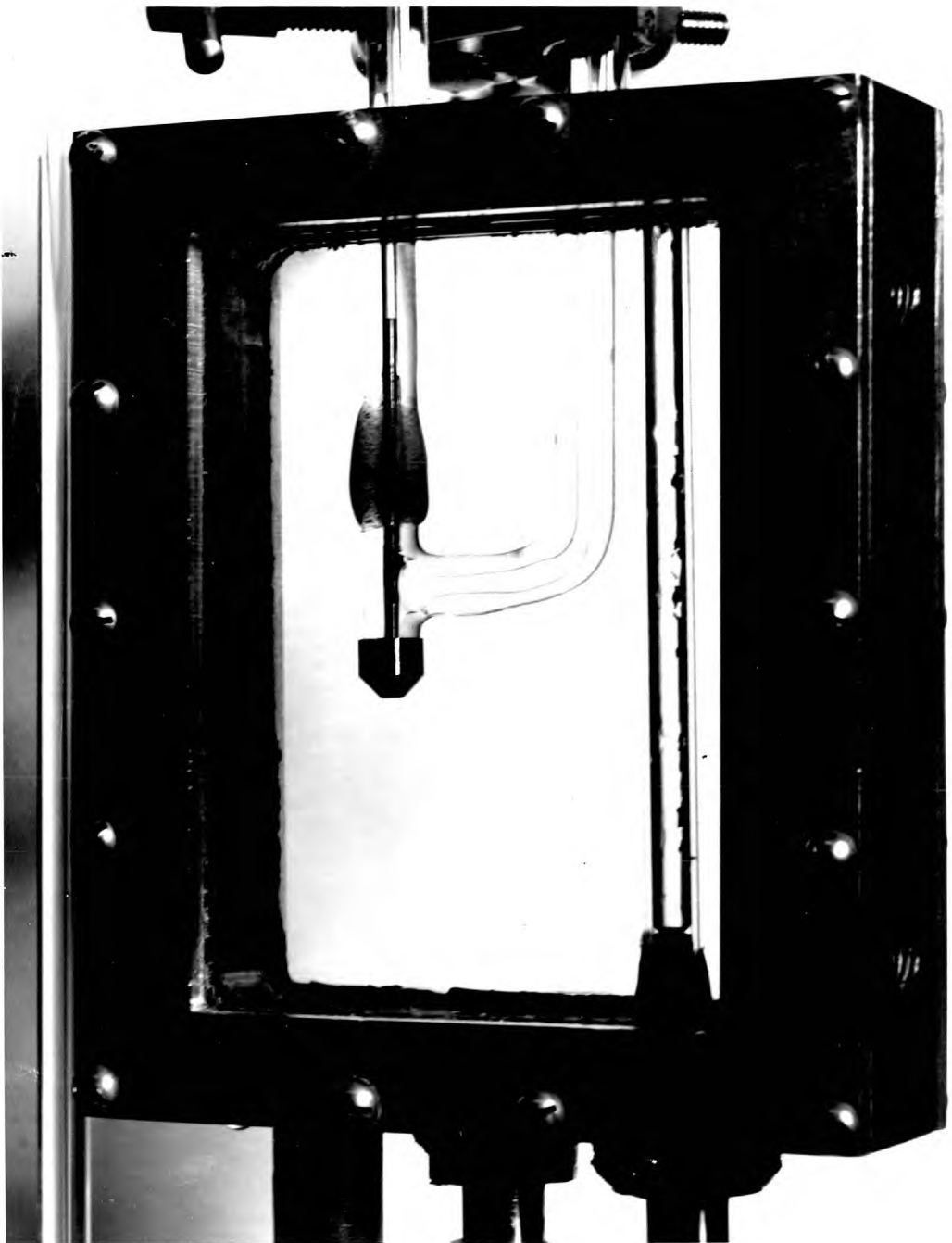


PLATE 5.2 : OBSERVATION CELL

6. EXPERIMENTAL PROCEDURE

6.1 Materials

The acetic acid, phenol and benzene used were of analytical reagent quality and were utilised as supplied without further purification. Water was ordinary laboratory distilled and before beginning each experiment both phases were mutually saturated. Five different surface active agents, all of which were soluble in the aqueous phase, were used and their specification is given below.

A. Dodecylamine Hydrochloride - $\text{CH}_3(\text{CH}_2)_{11}.\text{NH}_2.\text{HCl}$

A white crystalline solid, molecular weight 221.5, synthesised in the pure state and supplied by J.M. Barrell⁵⁹.

B. Teepol 514

A mixture of sodium secondary alkyl sulphates and sodium dodecyl benzene sulphonate in the ratio 60 : 40. Its molecular weight is 315 and it was ordinary commercial quality supplied by Shell Chemical Company Limited, in the form of a 27% by weight solution of active material.

C. Manoxol OT - Sodium dioctyl sulposuccinate

$$\begin{array}{c} \text{CH}_2\text{COOC}_8\text{H}_{17} \\ | \\ \text{CHCOOC}_8\text{H}_{17} \\ | \\ \text{SO}_3\text{Na} \end{array}$$

A white waxy substance, molecular weight 444, and supplied 100% pure by Hardman & Holden Limited.

D. Lissapol N - represented by the formula $R-O-C_2H_4(-OC_2H_4-)_nOH$ with a mean molecular weight of 572. An aqueous solution of an alkylated phenol-ethylene oxide containing a polyethylene glycol chain. It was of ordinary commercial quality supplied by I.C.I. Limited in the form of a 26.5% by weight solution of active material.

E. Sodium Lauryl Sulphate - $CH_3(CH_2)_{11}OSO_3Na$

A white powder of molecular weight 288. It was a general-purpose grade reagent supplied by British Drug Houses Limited.

6.2 Determination of Concentration

The concentration of solute in the benzene phase was determined with a high-accuracy Abbe refractometer. A sodium vapour lamp was used as a light source and all determinations were made at 25° C - ensured by means of a thermostatic control.

The refractometer was calibrated using standard solutions and the calibration curves are given in Figs. 6.1 & 6.2. From these curves the concentration corresponding to any refractometer reading can be obtained immediately.

Determinations of the concentrations of acetic acid in aqueous solution were carried out volumetrically, using a standard sodium hydroxide solution with phenolphthalein as indicator. As phenol is a solid at room temperature the concentration of its aqueous solutions was accurately known because of the gravimetric method of preparation.

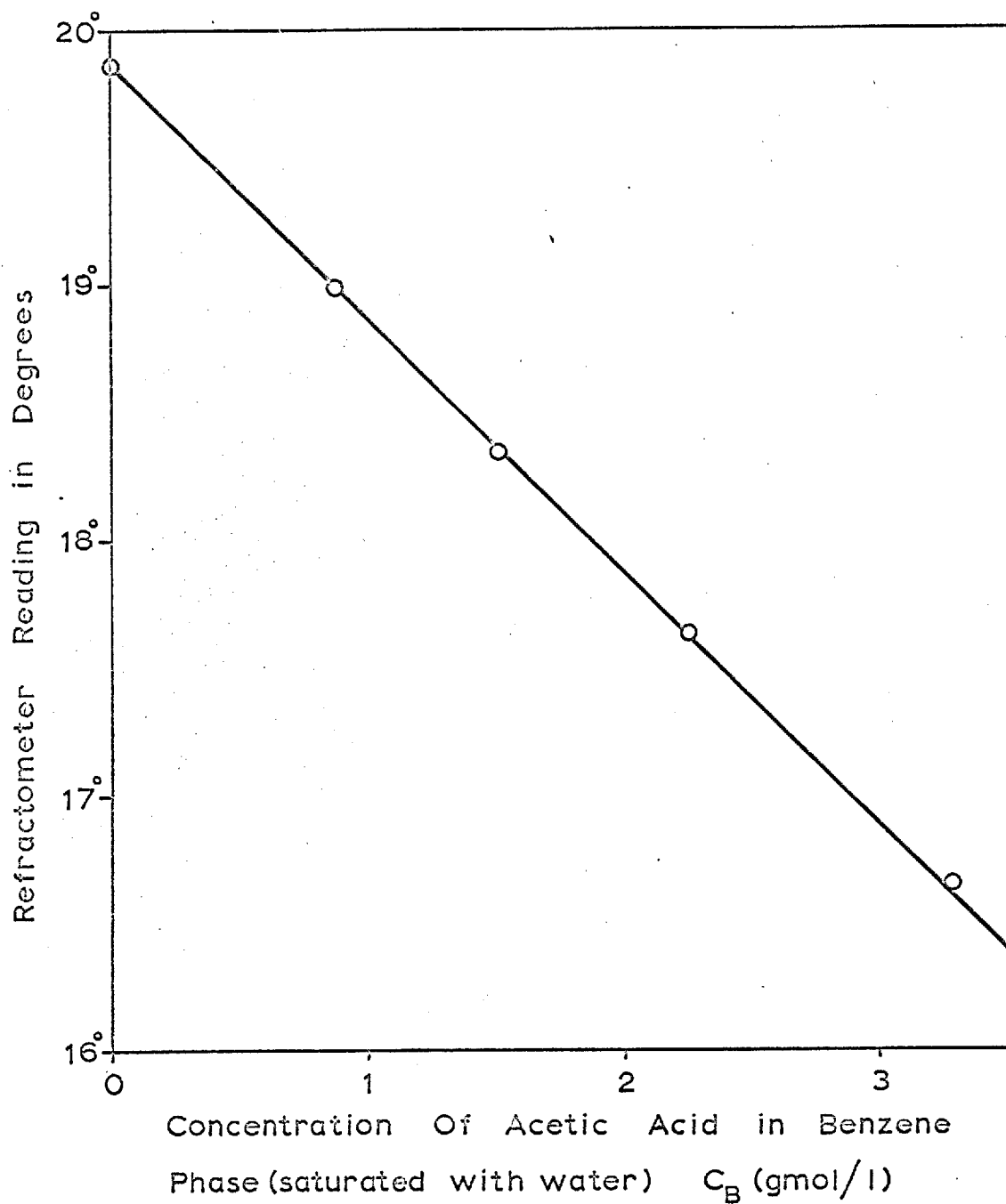


FIG.6.1: CALIBRATION CURVE FOR SOLUTIONS OF ACETIC ACID IN BENZENE AT 25°C

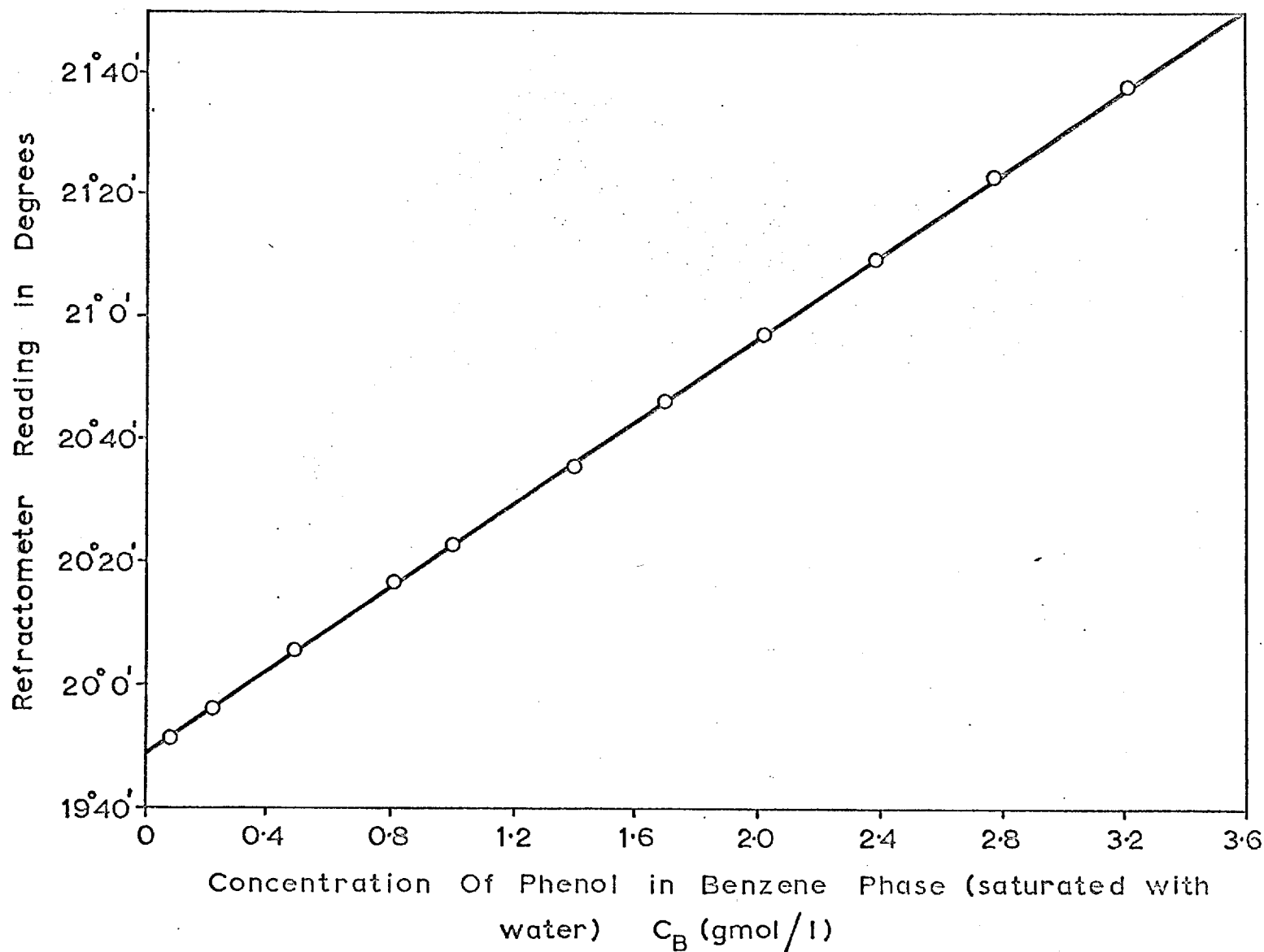


FIG. 6.2: CALIBRATION CURVE FOR SOLUTIONS OF PHENOL IN BENZENE AT 25°C

Standard solutions of each surface active agent were prepared and their densities determined using a specific gravity bottle. A known volume of this standard solution of surface active agent was then added to a known volume of the aqueous phase. Hence the molar concentration of surface active agent in the aqueous phase could be found.

6.3 Procedure

First, the nozzle and removable parts of the apparatus were thoroughly cleaned using, in order, chromic-sulphuric acid mixture, tap water and distilled water; with a final complete drying before re-assembly. The reservoir was filled with benzene phase and about 15 ml also placed in a small beaker which was raised under it until the nozzle tip was just submerged below the liquid surface. Then the pumps were started and, when liquid from the reservoir reached the nozzle, slight suction was applied to the vent tube (located at the right-angle bend just before the B7 socket into which the delivery side of the nozzle fitted). As soon as the nozzle and vent tube were completely filled with liquid the stopcock on the latter was closed. Pumping was continued until the outlet tube was filled with liquid and all air had been expelled from the apparatus. The position of the pump micrometer was then fixed at 2.00 and the motor speed adjusted to give a pump revolution time of approximately 3.5 seconds.

The aqueous phase, contained in a 2-litre aspirator fitted with a Mariotte tube to ensure a constant head, flowed to the observation cell by gravity. Its flow rate was controlled by means of a screw clip

and was measured by noting the volume collected in a given time.

In order that the nozzle could be immersed in the continuous phase contained in the cell, the beaker had to be removed. This could not be done without stopping the pumps, otherwise air was drawn into the apparatus. But it was necessary to stop the pumps only at the point where a drop was about to be formed by pump A, in which case, upon restarting the pump cycle began first with drop formation, and then followed withdrawal. The alternative of beginning with the withdrawal part of the cycle would have resulted in aqueous phase being sucked into the capillary tube.

Having stopped the pumps it was necessary - for reproducible drops - to ensure that upon immersion of the nozzle in the cell, it was wetted by the aqueous and not the benzene phase. Hence the nozzle was dried completely, great care being taken to avoid contamination with grease of any sort, for example, contact with the fingers.

After immersion of the nozzle the pumps were restarted and the position of the interface adjusted by means of the micrometer screw of the outlet pump B. The interface must be in the plane of the nozzle tip and was maintained there by successive adjustments throughout each run.

45 minutes were allowed to elapse before the first sample was taken and thereafter samples of approximately 0.2 ml were taken at

five-minute intervals and analysed with the refractometer. Sampling was continued until seven consecutive samples gave consistent results, i.e. steady conditions existed for 30 minutes.

During each run the pump speed was determined by timing 20 strokes, a measurement which was frequently repeated, as was the flow rate of the aqueous phase.

For each run a record was kept of the visual observations of the interface of the drop and in particular the type of transfer which occurred.

6.4 Results

For every run the concentrations of solute in the benzene phase were determined before and after extraction.

The aqueous phase was analysed before each run but its concentration was assumed to remain constant. This may be justified by the fact that the flow rate of the aqueous phase was much larger than that of the benzene phase, namely about 20 ml/min compared with 0.7 ml/min.

The flow rate of the aqueous phase and time for one complete revolution were noted, the drop volume being kept constant throughout at 0.4 ml (corresponding to pump micrometer position 2.00) The experimental results are given in Tables I & II of Appendix B

7. EQUILIBRIUM DATA

7.1 Determination of Solute Concentration

(a) Acetic Acid Concentrations of aqueous solutions of acetic acid were determined volumetrically using standard sodium hydroxide solution with phenolphthalein as indicator; concentrations of acetic acid in benzene were determined with the refractometer.

(b) Phenol The concentration of phenol in the benzene phase was also determined with the refractometer.

The concentration of phenol in the aqueous phase was found in two ways:

(i) The initial concentration of phenol in the aqueous phase was accurately determined gravimetrically, for phenol is solid at room temperature. The initial concentration of phenol in the benzene phase was zero. Thus, the amount of phenol in the aqueous phase after contacting and separation was found from a measurement of the increase of concentration of phenol in the benzene phase.

(ii) As a check for the above method, the actual concentration of phenol in the aqueous phase, after contacting and separation, was determined by the bromine method.⁶⁰ An aliquot of sample was taken - estimated to contain about 0.02 gm of phenol - and transferred to a 500 cc glass-stoppered flask. Next distilled water was added to make the volume up to approximately 200 cc, then 25 cc of potassium bromide solution containing 250 gm/litre. The flask was then allowed to stand until the temperature reached 25°C before 25 cc of potassium bromate solution, containing 3 gm/litre, was added. The contents of the flask were

thoroughly mixed and, with the temperature maintained at 25°C, were allowed to stand for 30 minutes, the flask being shaken two or three times during this period. At the end of this time 25 cc of potassium iodide solution, containing 200 gm/litre, were added and the contents thoroughly mixed, the flask again being allowed to stand for 30 minutes, with intermittent shaking.

The liberated iodine was titrated with 0.1 N sodium thio-sulphate solution, starch being added near the end point. Any return of the blue iodine-starch colour was disregarded. A blank determination was performed in the same manner.

The number of moles of phenol present in the aqueous sample is then given by

$$\text{No. of moles of phenol} = \frac{\text{Titration difference (ml)} \times \text{normality of thiosulphate}}{6 \times 10^3}$$

7.2 Experimental Procedure

The reagents were placed in a 100 ml glass-stoppered conical flask in quantities estimated to give a set of points over a variable range of acetic acid or phenol concentration; for the latter determinations the initial concentration of phenol in the aqueous phase was accurately known. The mouths of the flasks were then waterproofed by covering with polythene sheet and rubber bands, and the flasks immersed in a thermostat bath maintained at 25°C. They were then shaken at a speed great enough to disperse the two phases in one another. After

shaking the phases were allowed to settle for an hour and samples were analysed. The shaking and sampling procedures were repeated until no further concentration changes were detectable.

7.3 Results

The experimental values are given in Tables I & II of Appendix C and are shown graphically in Figs. 7.1 & 7.2. The data of Brown and Bury⁶¹, Bektourov⁶² and Herz & Fischer⁶³ for the equilibrium between benzene-acetic acid-water at 25°C are in agreement with those obtained and are shown in Figs. C.1 & C.2 of Appendix C. The data of Rothmund & Wilsmore⁶⁴, Philip & Clark⁶⁵ and Nagata & Eguchi⁶⁶ for the equilibrium between benzene-phenol-water at 25°C are in good agreement with those obtained and are shown in Figs. C.3 & C.4 of Appendix C.

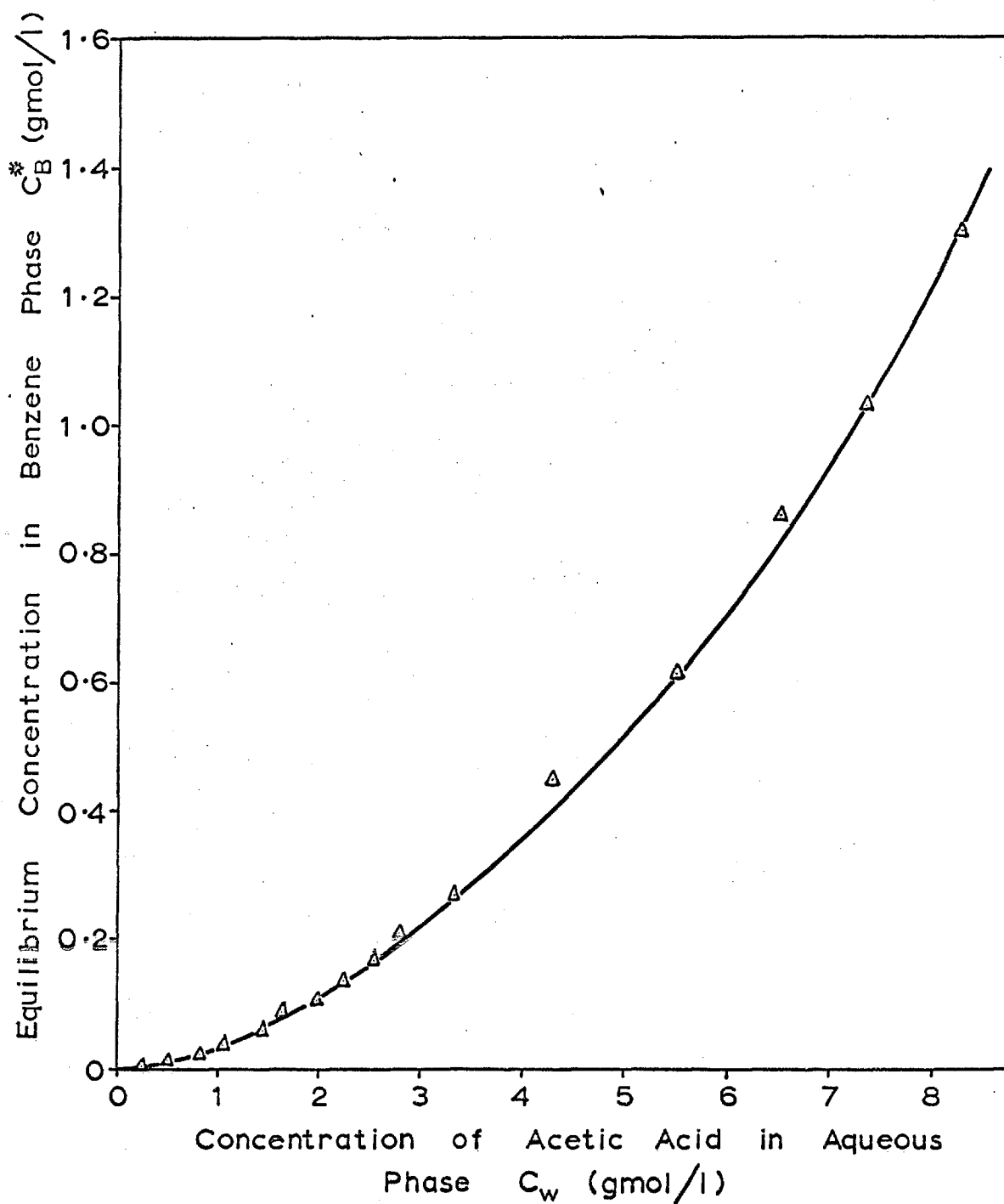


FIG.7.1: EQUILIBRIUM CURVE FOR BENZENE-ACETIC ACID-
WATER SYSTEM AT 25°C

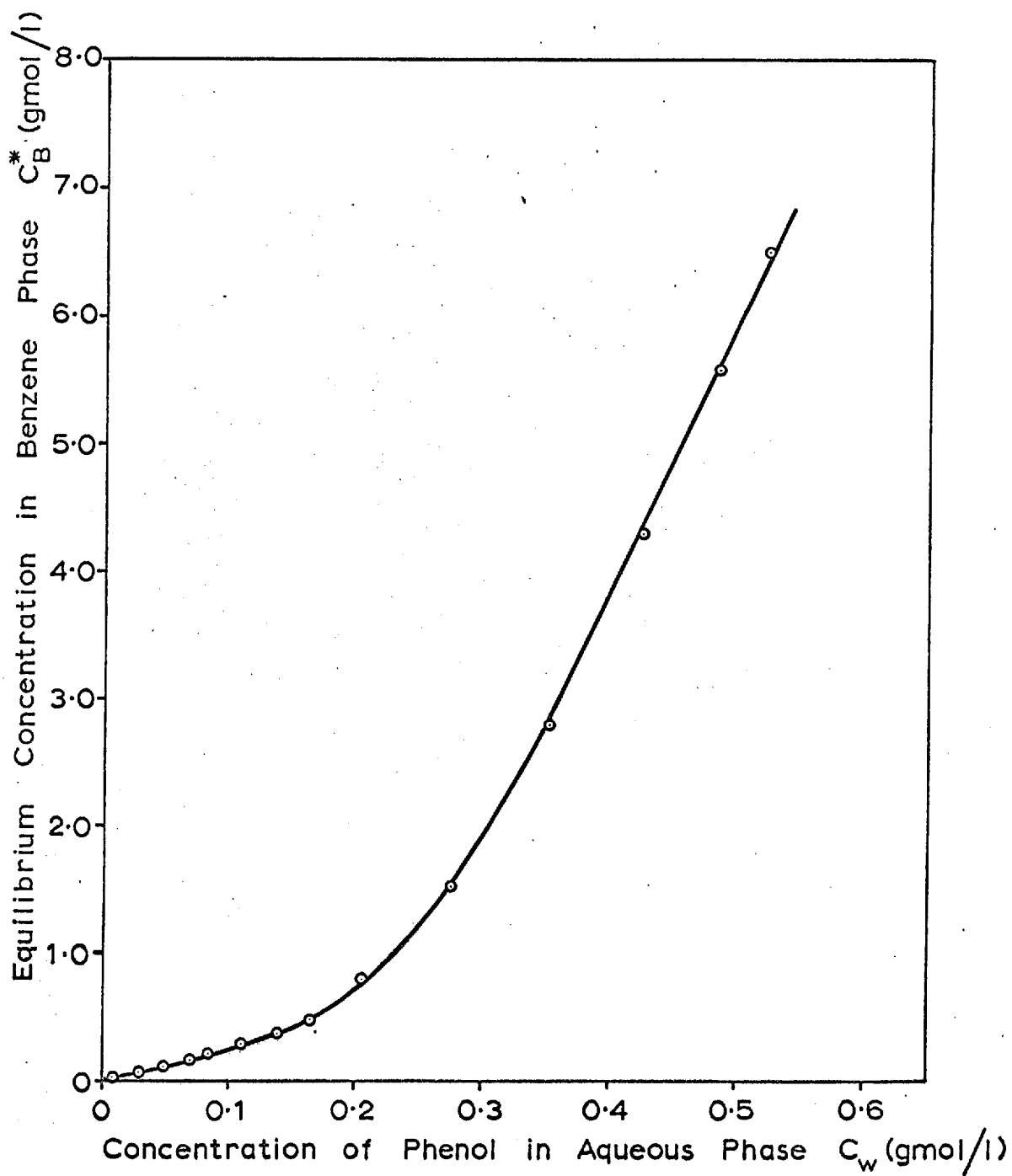


FIG.7.2: EQUILIBRIUM CURVE FOR BENZENE-
PHENOL-WATER SYSTEM AT 25°C

8. INVESTIGATION OF SURFACE PROPERTIES

The investigation is concerned with the manner in which the surface properties influence the hydrodynamic conditions at an interface, and hence the mass transfer rate across the interface.

The interface between two liquids cannot be considered as a geometric plane; it possesses a small but finite thickness and there are forces existing there which are different from those in the bulk phases. Should the equilibrium of forces existing in the interface be disturbed in any way, movements may occur in the interface (Marangoni effect) until the equilibrium is restored.

The important surface property directly linked with this effect is that of surface pressure, π . This can be regarded as the two-dimensional pressure of the molecules of the surface film, partially offsetting the contractile tendency in the interface. Its value is given by $\pi = (\sigma_0 - \sigma)$, where σ_0 is the interfacial tension in the absence of solute or surface active agent and σ is the interfacial tension in the presence of either of them. It is an accepted fact that the cause of movements in the interface is the presence of surface pressure gradients set up there as the result of local concentration fluctuations, which themselves arise from liquid movements in the bulk phases. The resultant force arising from these surface pressure gradients will tend to restore the equal surface distribution of solute or surface active molecules by displacement in the plane of the interface.

The magnitude of this displacement produced by the surface force is determined by another important surface property, that of surface compressibility. The compressibility of a surface is the fractional decrease in the surface area per molecule caused by unit surface pressure difference, and can be expressed by means of the surface compressional modulus M , defined as

$$\frac{1}{M} = - \frac{1}{A} \frac{dA}{d(\Delta\pi)} \quad \dots \quad 8.1$$

where $\Delta\pi$ is the surface pressure difference and A is the area available to each molecule in the surface film. M has the same units as σ (interfacial tension) and π , i.e. dynes/cm. If M is large the film is almost incompressible and very large forces are involved if the film is compressed further or allowed to expand. If M is small the film is easily compressed and small forces are involved.

The surface compressional modulus M is analogous to Young's Modulus of elasticity E_y given by Hooke's Law, which states that, within the elastic limit, a strain is proportional to the stress producing it, i.e.

$$E_y = \frac{\text{stress}}{\text{strain}} \quad \text{for a given material}$$

Hence the ratio $\Delta\pi/M$, i.e. surface pressure difference or "surface stress" to the surface compressional modulus, will give the extent to which the interface can be "strained".

However, the surface compressibility gives only an indication as to the extent to which the surface can be compressed, it gives no

indication as to the rate of compression. The rate of compression will be affected by another important surface property, that of a two-dimensional or surface viscosity. This property may augment the effect of the surface compressional modulus in preventing liquid movements near the interface.

There are two kinds of surface viscosity: (a) the surface shear viscosity which may restrict motion by resisting two-dimensional shear in the plane of the film itself, and (b) the surface compressional viscosity which may restrict motion by presenting "resistance" to compression in the plane of the film itself.

The surface compressional viscosity cannot be measured experimentally and the investigations have, therefore, been restricted to the experimental determination of the surface shear viscosity (henceforth referred to simply as the surface viscosity). Thus, the surface viscosity is a measure of the resistance of the surface film to shear in the plane of the surface. It has dimensions MT^{-1} and is measured in units of gm/sec, called "surface poises" (sp).

The importance of surface pressure gradients as controlling factors in the rate of mass transfer from liquid drops has been recognised by Linton & Sutherland⁶⁷. Levich⁶⁸ has stressed the hydrodynamic importance of surface tension forces but does not appear to refer to the surface compressibility as such, in the above connotation, although he later attributes the damping of ripples by

surface active agents to the surface modulus which he refers to as "a coefficient of elasticity of the Film". Stuke⁶⁹ in his paper on the "Flow Behaviour of Interfaces" has recognised all of the above-mentioned surface properties, including the two kinds of surface viscosity, and gives an account of the hydrodynamic properties of interfaces. Davies & Mayers⁵⁰ have investigated the effect of surface shear viscosity (they make no mention of surface compressional viscosity) and surface compressibility on mass transfer rates in a stirred cell, for the case of insoluble surface active agents such as plasma, albumen and protein.

In the present work the respective influence of these surface properties on mass transfer rates has been examined, first for the case of soluble surface active agents and then, more generally, it has been extended to solutes.

9. SURFACE VISCOMETRY

9.1 Survey

The most accurate method of obtaining the viscosity of an insoluble monolayer spread at an air-water interface is to cause it to flow (under the influence of a surface tension gradient) through a narrow canal placed in the surface. Under these conditions an accurate allowance can be made for the drag on the surface film exerted by the underlying liquid^{70,71}. Joly⁷², Nutting & Harkins⁷³ and Ewars & Sack⁷⁰ report a variety of results for both soluble and insoluble films. Applied to soluble adsorbed films this method suffers from the disadvantage that the gradient of surface tension (or surface pressure defined as the lowering of surface tension caused by the monolayer) causes desorption and adsorption to occur, as well as flow through the canal.

Another type of surface viscometer widely used is that employing the rotational torsional method^{74,75}. With this instrument a steady rotation of the liquid surface against a stationary disc placed in the surface produces a measurable torque from which the surface viscosity is calculated. Although this instrument is widely used there are three limitations to its sensitivity and accuracy. First, the correction is rather high for the torque of the clean water surface (and the immediately underlying water) on the disc. Secondly, addition of surface active agents can alter the water level slightly, by altering the form of the menisci⁷⁴. This slightly increases the depth of immersion of the disc and hence may lead to increased drag from the

underlying water. Finally, the formula used to calculate the surface viscosity is based on the assumption that the movement of the underlying water is the same whether a film is present or not, i.e. the film slips freely over the water. Davies⁷⁶ has shown that there is no slippage between the monolayer and the bulk liquid adjacent to it. The monolayer actually adheres to the water and therefore the measured torque is higher than would be found for the monolayer alone. The derived viscosities are thus too high, as has been pointed out by Ewars & Sack⁷⁰.

Another method of measuring the surface viscosity of adsorbed or spread films employs a moving liquid substrate to cause the film to flow through a stationary canal in the surface. This is known as the "viscous traction" method. The movement of the film in the canal (shown with talc particles) depends partly on the viscous traction of the subjacent layers of bulk liquid; this traction tends to move the film in the canal at the speed of the liquid. However, this is opposed by the drag of the stationary walls on the canal acting on the viscous monolayer, and from the movements of the talc particles the surface viscosity may be calculated. There are two principal types of viscous traction surface viscometers. The first of these employs a linear canal and although it is suitable for insoluble monolayers, applied to soluble adsorbed films it suffers from the disadvantage that the gradient of surface pressure causes desorption and adsorption to occur, and it is extremely difficult to correct for these effects^{70,77}. To deal more simply with soluble adsorbed films Davies⁷⁸ has devised a

circular viscous traction viscometer. This instrument consists of two concentric stationary cylindrical knife edges, with a narrow annulus between them. The knife edges touch on to the film surface as it rotates in a concentric dish containing the substrate. Thus, a narrow canal is formed in which the film is observed by sprinkling talc particles on to the liquid surface. The retardation of the talc, caused by the adsorbed or spread film, is a measure of the surface viscosity of the film. The big advantage for soluble films is that there is no surface pressure gradient set up, therefore adsorption and desorption need not be considered. The instrument must be calibrated using films of known surface viscosity, obtained by the canal method^{72,79,80} in which corrections have been made for the lack of slippage between the monolayer and the water.

Early work on the determination of interfacial viscosities between two liquids was carried out with oscillating needles or discs, although the presence of the second bulk phase so reduces the sensitivity that viscosities below about 1 sp cannot be measured^{81,82}. Also, this method is subject to the inaccuracies mentioned previously, under rotational torsional methods. Recently Davies & Mayers⁸³ have modified the viscous traction method devised by Davies⁷⁸, to enable the interfacial viscosity of spread or adsorbed films to be measured at oil-water or air-water interfaces. They give results mainly for insoluble films - such as plasma albumen protein - spread at oil-water interfaces.

In this work an examination has been made first of soluble surface active agents and more generally it has been extended to solutes.

9.2 Construction and Calibration of Surface Viscometer

A circular viscous traction, or ring, viscometer has been constructed for the investigation of interfacial viscosity and it is shown diagrammatically in Fig. 9.1 Plate 9.1 shows a photograph of the instrument with the rings lying in the benzene-water interface. The main feature is a pair of stainless steel rings which are coplanar and concentric. They are of rectangular cross-section and were made by turning two annuli from 0.056 cm sheet. The diameters of these rings were such that they were each 0.08 cm in width, and between them defined a canal of inner and outer diameters 11.20 cm and 12.15 cm respectively, that is to say a canal width of 0.475 cm. Three support wires were fixed to each of the rings at approximately 120° intervals, and these in turn were fixed to more rigid vertical support rods, as shown in Fig. 9.1, each threaded and shouldered at their upper ends. To give some degree of flexibility of movement in the vertical plane, and thereby allow for accurate alignment, small springs are placed on the shoulders before passing the rods upwards through a support plate, where they are retained by nuts on the upper side. This constructional arrangement can be seen in Plate 9.1. Movement in the horizontal plane was allowed for in the support plate itself, simply by enlargement of the holes through which the support rods passed. Great care was taken to ensure that the assembled rings were closely

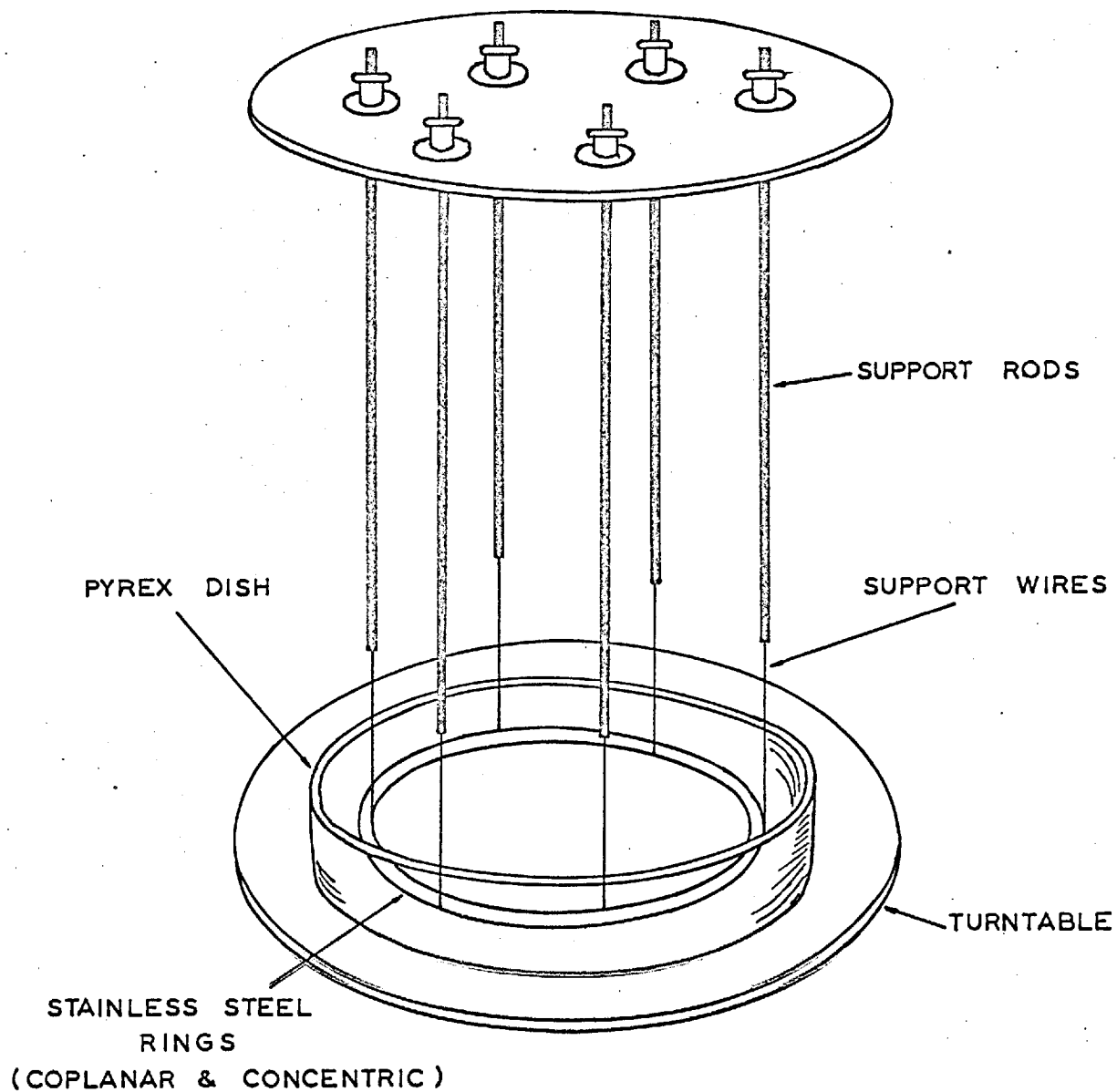


FIG. 9.1: SCHEMATIC DIAGRAM OF
SURFACE VISCOMETER

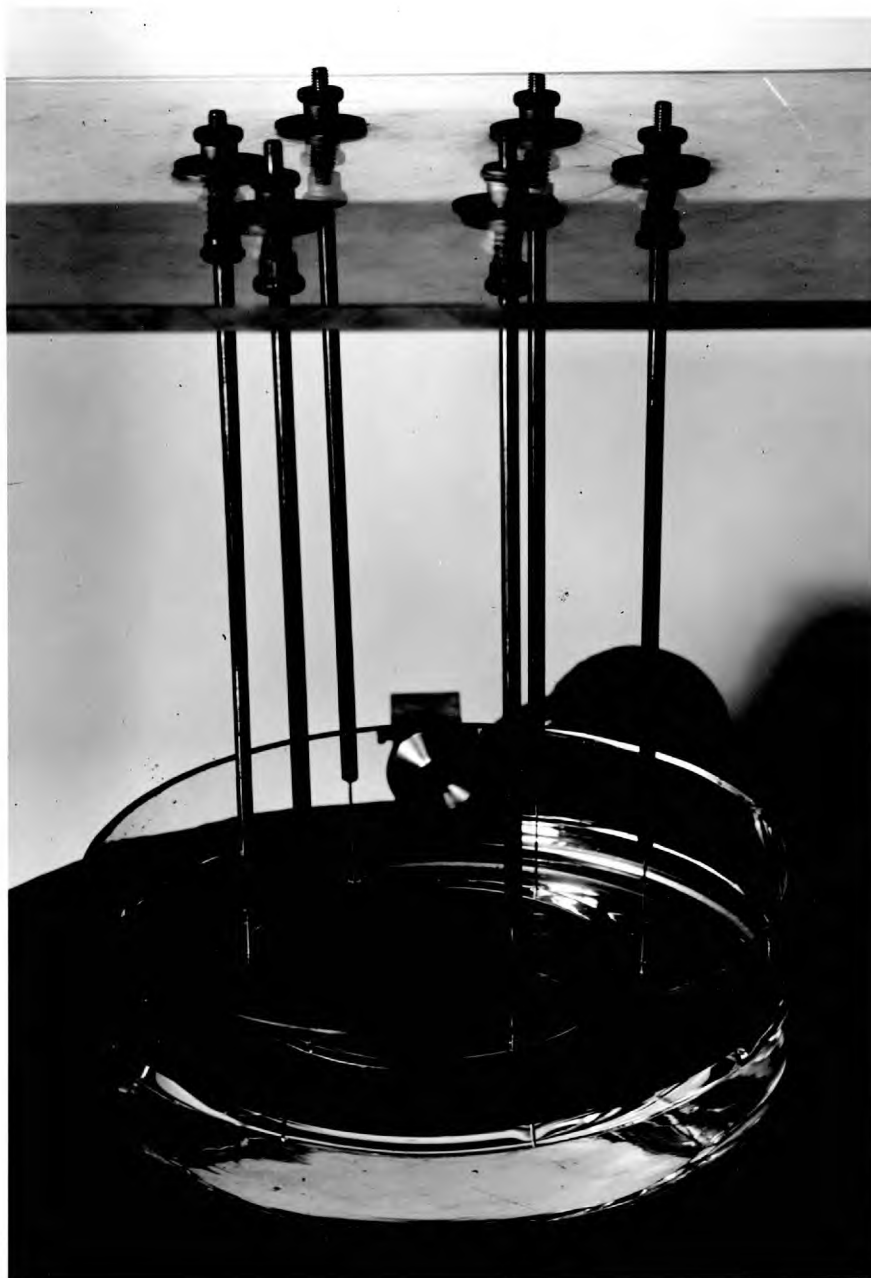


PLATE 9.1: PHOTOGRAPH OF SURFACE VISCOMETER
WITH RINGS LYING IN OIL-WATER INTERFACE

concentric and coplanar, so that the canal formed between them was of uniform width. The whole assembly was supported on a metal framework contained in a windowed box, to prevent dust from contaminating the apparatus and allow for its observation when in use.

At the beginning of a calibration run the whole assembly was lifted from its box in order to clean the rings; first with chromic-sulphuric acid mixture, then tap water followed finally by distilled water. At the same time a Pyrex glass dish (of inner diameter 20.2 cm and depth 6.3 cm) was thoroughly cleaned and placed centrally on the turntable. This was filled to a depth of 2.5 cm with aqueous phase which had previously been maintained thermostatically at 20°C. The liquid surface was spread with ignited talc and then sucked clean by means of a capillary connected to a small vacuum pump (a cleansing operation to remove any stray surface active impurities). The ring assembly was then returned to the shielding box, but first the turntable height was adjusted (by means of the four levelling screws at each corner of the baseplate) to make sure that the rings did not reach the liquid surface. Then the turntable was raised from below so as to contact the liquid surface with the rings, and adjusted to such a position that the meniscus within the canal was slightly concave upwards. This ensured that the talc particles sat in the centre of the canal and could therefore be readily timed. To minimise any oscillations of the rotating turntable in the horizontal plane, it was supported at its circumference by two pulley wheels in contact with it from above and below, each wheel carrying O-rings as "tyres". The

turntable was driven by a constant speed motor, and with suitable reduction gearing made one revolution every 38 seconds. Set in motion, it was then necessary to measure the time of revolution of a talc particle at the centre of the canal. For this clean surface the average time for one revolution was found to be 98 seconds.

In order to calibrate the instrument insoluble films of pure octadecyl alcohol and pure stearic acid were applied from petroleum ether solutions. The solutions were injected in small amounts at various points in the interface by means of the needle of a microsyringe, the needle having previously been contacted with a separate clean water surface to remove any excess solution from its tip. Joly⁷² has determined the surface viscosities for these films at various standard areas per molecule and these viscosities are given in Table I of Appendix D. During the film spreading operation the turntable was lowered and after completion raised again to bring the canal rings into contact with the liquid surface. A small correction had to be made for the film area on account of the small surface area now being covered by the stainless steel rings. The revolution times of the talc particles in the centre of the canal, in the presence of films of known surface viscosity, were noted (the average of three or four complete revolutions or a half or one revolution for the very long times). Each experiment was repeated at least twice and the results were recorded as "retardations", the difference in revolution times for a talc particle on a monolayer and on a clean surface. The calibration curve for the viscometer is shown in Fig. 9.2; the experimental results

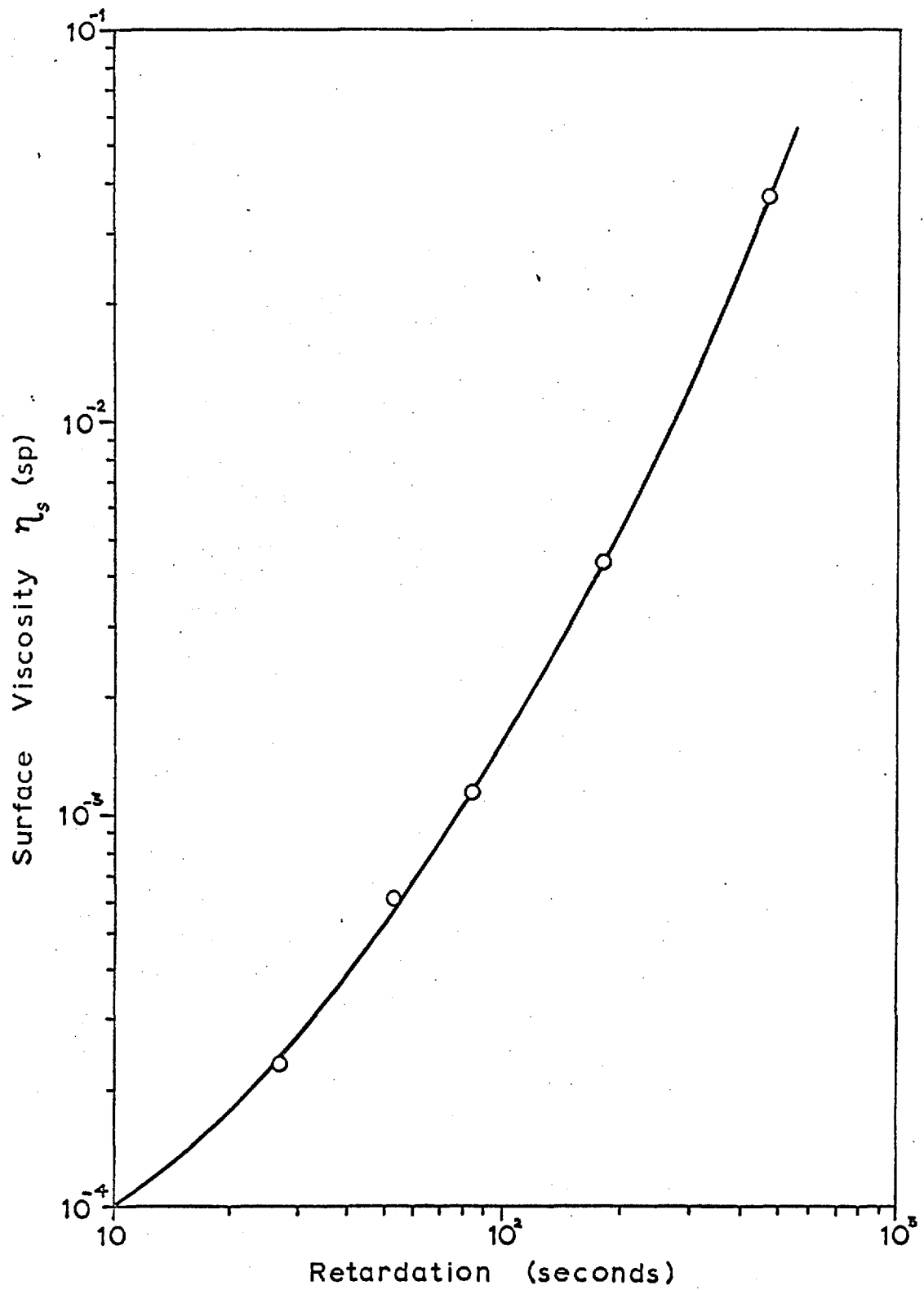


FIG. 9.2: CALIBRATION CURVE FOR SURFACE VISCOMETER

being given in Table I of Appendix D.

By a fortunate coincidence, when benzene is used as the organic phase the retardation of a talc particle in the clean interface was almost the same as that in the canal at the air-water interface. Rotation times of 106 seconds and 98 seconds respectively were recorded when the dish was rotated once in 38 seconds. For the water-ethyl acetate interface the time was 101 seconds. The approximate equality of the revolution times of the clean air-water and oil-water interfaces in the canal implies that the viscous drag which the rotating oil exerts on the talc in the canal balances the extra drag exerted on the interface by the stationary canal walls via the adjacent oil. Consequently the same calibration curve can be used as for the air-water surface.

The ring viscometer is sensitive to 1.10^{-4} sp, although its sensitivity may be increased or decreased by decreasing or increasing the width of the canal respectively. By using different speeds of rotation, the shear rate could be varied; calibration curves of films whose behaviour was known to be purely Newtonian would be required. One could then use the apparatus to study surface or interfacial films of which the viscosity was a function of the shear rate.

9.3 Experimental

In order to investigate the variation of surface viscosity with concentration of the surface active agent, known amounts of the standard solutions of the surface active agents were added to the

aqueous phase and the retardation time for the talc particle was recorded for each different concentration in the aqueous phase. For the case of solutes the variation of surface viscosity with concentration was determined as follows. Solutions containing equilibrium concentrations of solute in the aqueous and benzene phases were contacted - in a thermostat bath - and left until equilibrium had been fully established. The phases were then separated, the concentration of solute in each checked, and were then used in the viscometer giving a particular values for the retardation time of the talc particle. The procedure was then repeated for different solute concentrations in the phases.

Before each experiment all liquids were brought to 20°C and the apparatus was scrupulously cleaned with chromic-sulphuric mixture.

9.4 Results

For every run the concentrations of surface active agent or solute in both phases was noted, together with the revolution time of the talc particles (the average of 3 or 4 revolutions). The readings are tabulated in Table II of Appendix D. Figs. 9.3 & 9.4 show the variation for the solutes acetic acid and phenol respectively. The curves for the surface active agents are similar in shape and to avoid repetition in this part of the text only one is shown, Fig. 9.5; the rest are given in Figs. D.1 to D.4 of Appendix D.

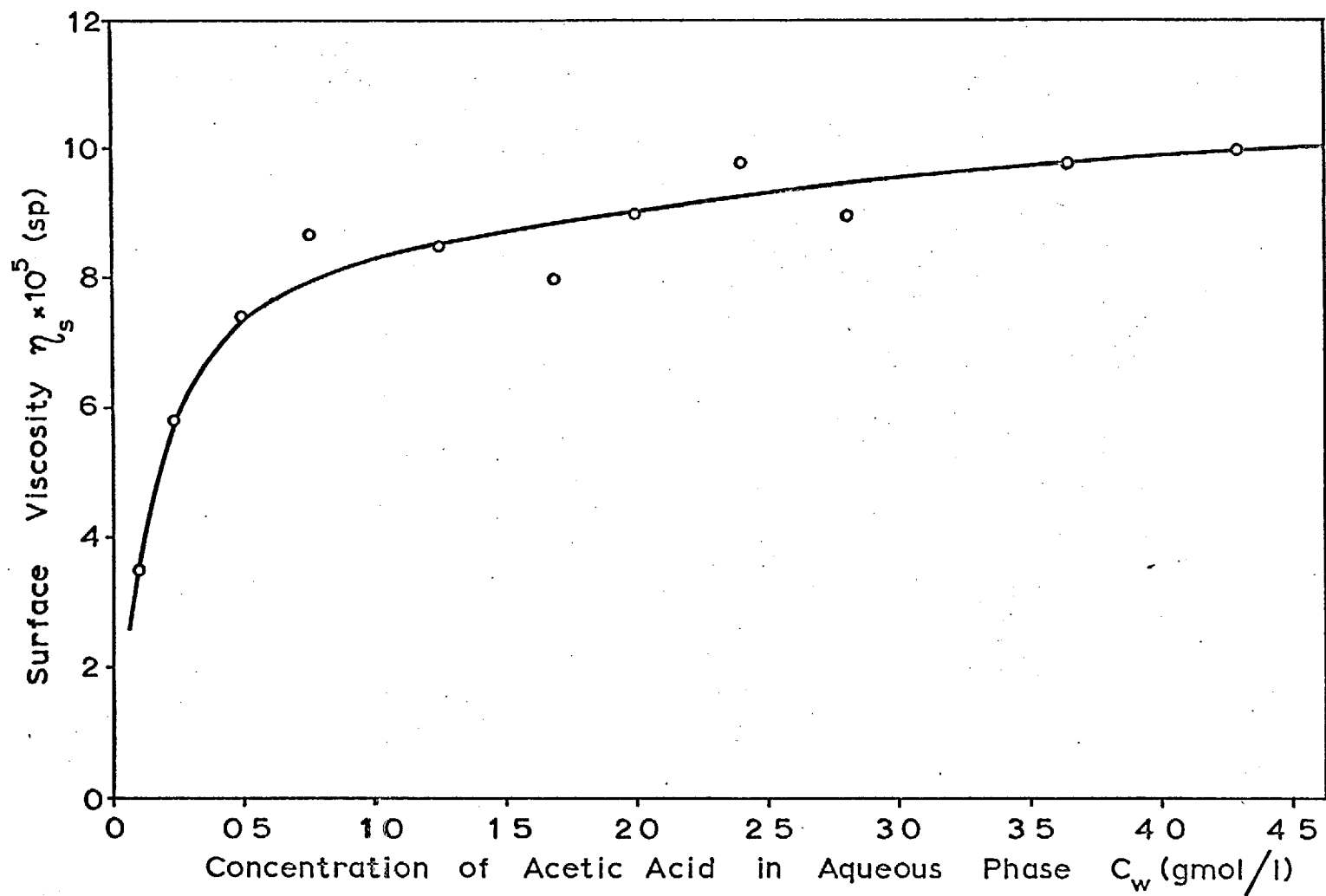


FIG.9.3: VARIATION OF SURFACE VISCOSITY WITH CONCENTRATION OF ACETIC ACID IN AQUEOUS PHASE

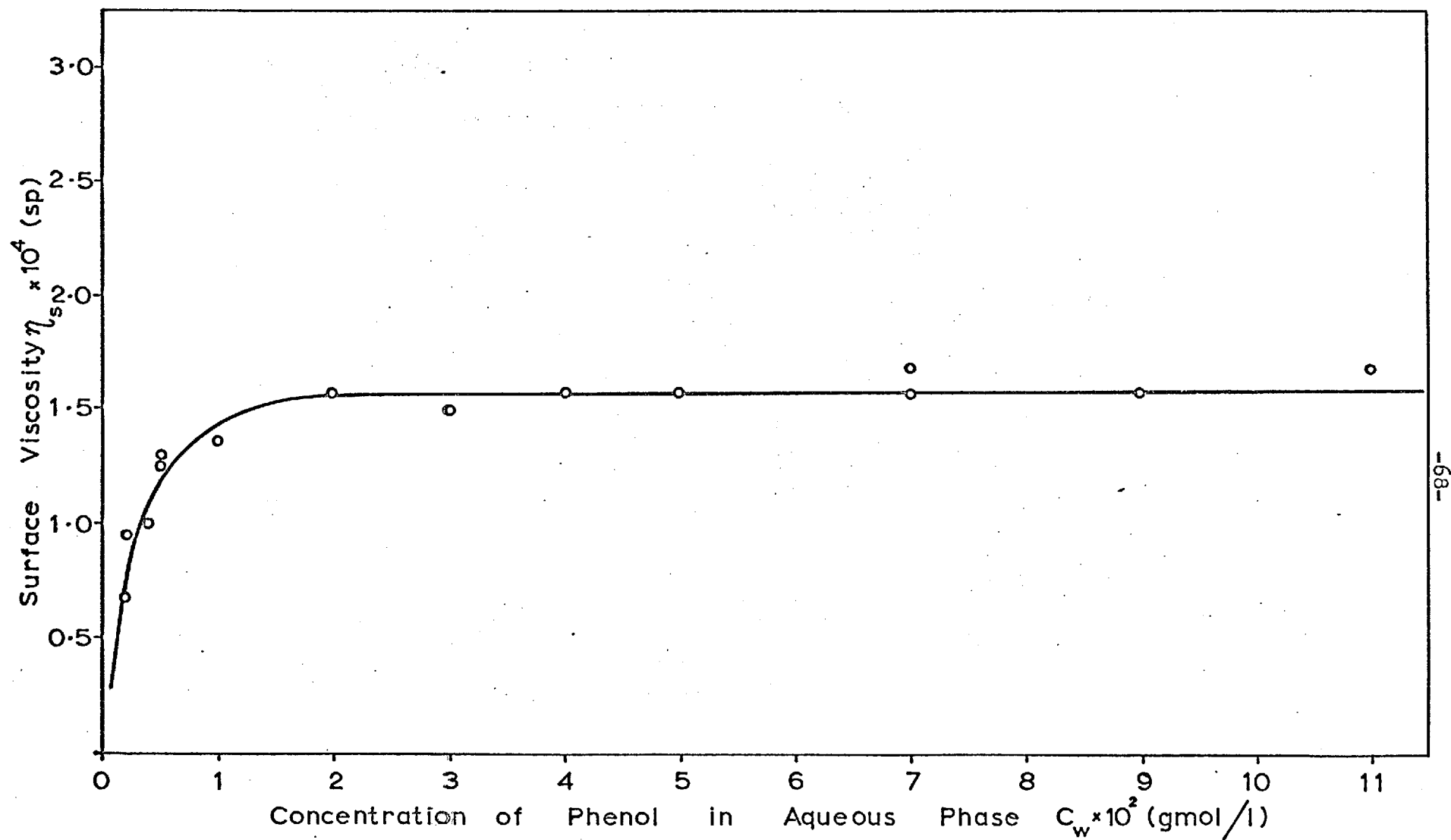


FIG. 9.4: VARIATION OF SURFACE VISCOSITY WITH CONCENTRATION OF PHENOL IN AQUEOUS PHASE

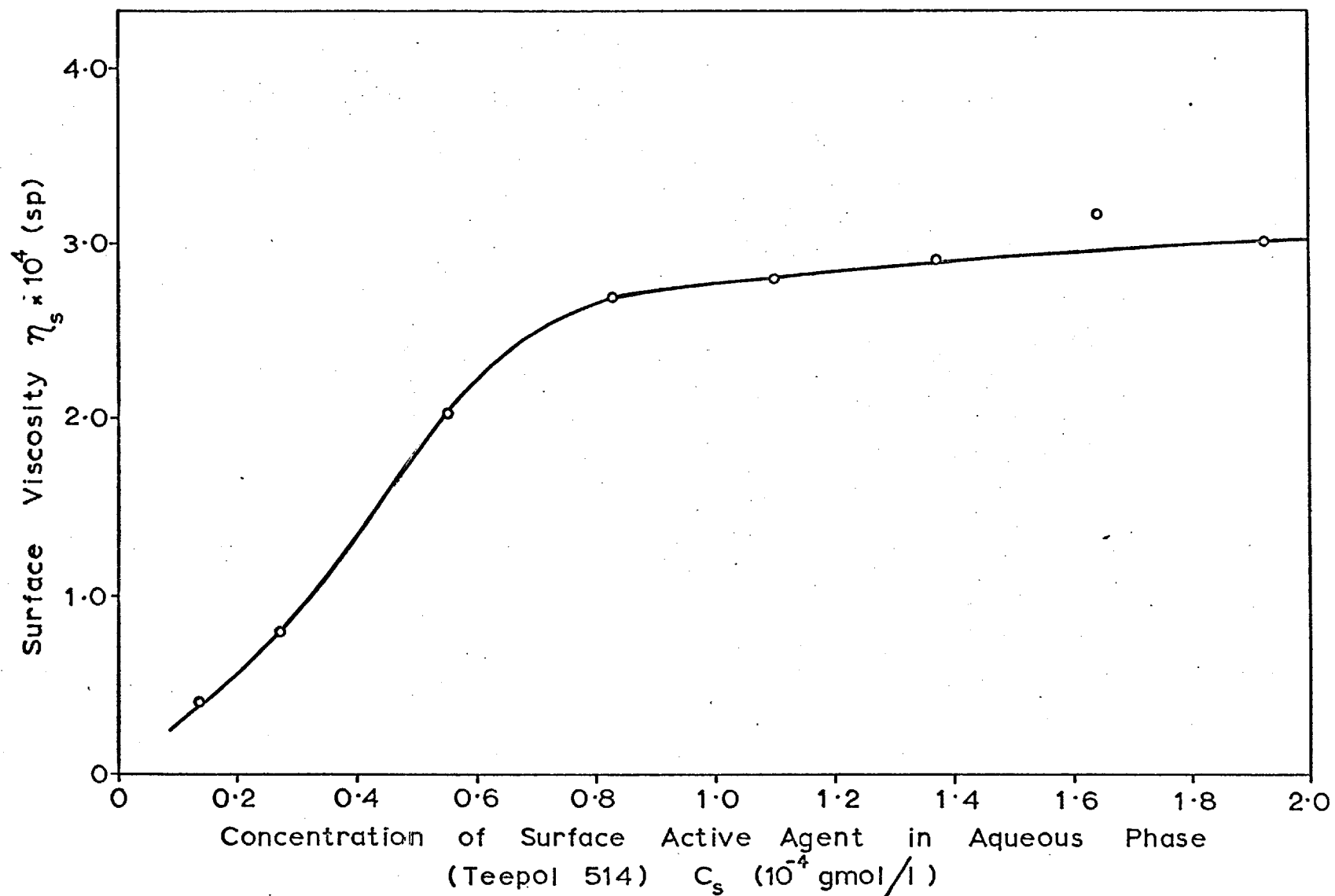


FIG.9.5: VARIATION OF SURFACE VISCOSITY WITH CONCENTRATION OF SURFACE ACTIVE AGENT TEEPOL 514.

10. INTERFACIAL TENSION AND ITS MEASUREMENT

10.1 Apparatus and Procedure

Determinations of interfacial tension as a function of solute/surface active agent concentrations were carried out using the drop-weight volume method, the apparatus used being shown in Plate 10.1. It comprises a capillary U-tube A B C D with a bend at D. One of the arms, A B C, is graduated and contains in it a small bulb B, the volume of the bulb between two zero marks on the graduated scale being accurately known - 2.343 ml. A glass tip of known diameter - 0.660 cm - is fixed to the end of the capillary at E by means of a B7 cone and socket. The tip is contained in a glass vial F which is kept in position by means of the brass support plate shown. The whole apparatus can be supported in a thermostat bath by means of the rod H.

Special precautions were taken to ensure that the glass tip was ground flat. A piece of Veridia precision tubing was joined to a B7 socket. Using a travelling microscope, the glass tube was positioned vertically. It was then surrounded by a 1" diameter brass cylinder with machined ends. The annulus between the cylinder and the glass tubing was filled with molten paraffin wax and allowed to set. The glass tip and brass cylinder were then together ground away with carborundum powder until the glass tip was flat and sharp edged.

The aqueous phase of known solute or surface active agent concentration was sucked up into the pipette A B C D, this phase being used since it will preferentially wet the glass. The organic phase,

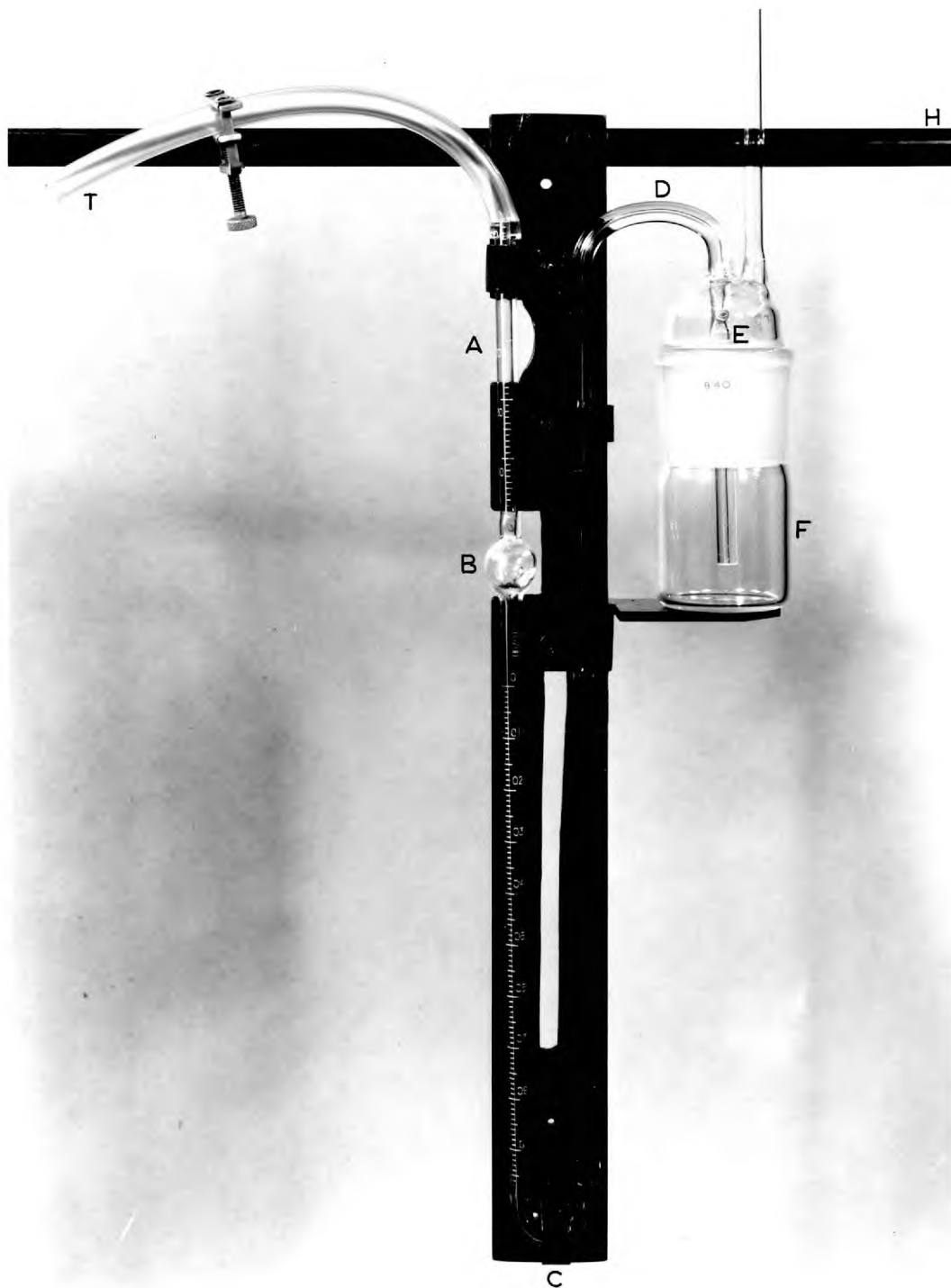


PLATE 10.1 : APPARATUS FOR MEASURING
INTERFACIAL TENSION

which was in equilibrium with the aqueous one, was poured into the glass vial F and placed beneath the glass tip so that it was just submerged in the organic liquid. The vial was then fixed in position by means of its brass support plate and the whole apparatus immersed in a thermostat bath at 25°C. By means of the tubing T the interface of the aqueous phase in the glass tip was adjusted so that it was in the same plane as the tip, the reading on the graduated capillary scale being noted. Drops were then formed slowly (not faster than one every 3 minutes) by application of slight pressure via the tubing T. Special care was taken to ensure that the detachment of the drops occurred very slowly. Drops were formed until the level of the aqueous phase fell below the bulb B, when the pressure was removed, the position of the interface adjusted and the liquid level noted. Hence, from a knowledge of the number of drops formed and the difference of readings on the graduated capillary, a mean drop volume was deduced.

To allow for the fact that the liquid forming the drop does not completely leave the tip, a correction factor given by Harkins⁸⁴ was applied, $f(r/\sqrt[3]{V})$. This function is shown in Fig. 10.1. and depends solely on the ratio of the radius of the glass tip to the cube root of the drop volume.

The densities of the aqueous and organic phases were determined with the use of a specific gravity bottle, and from a knowledge of these densities, the drop volume and correction factor, the interfacial tension was calculated using the equation -

$$\sigma = \frac{V(\rho' - \rho'') g}{2\pi r f(r/\sqrt[3]{V})} \quad \dots \quad 10.1$$

where σ = the interfacial tension, in dynes/cm.
 ρ', ρ'' = densities of heavier and lighter phases respectively in gm/cm³.
 g = the acceleration due to gravity, in cm/sec²
 r = the radius of the glass tip, in cm.
 V = the drop volume, in cc.
 $f(r/\sqrt[3]{V})$ = the correction factor given in Fig. 10.1.

10.2 Results

The experimental values are given in Table I of Appendix E. Figs. 10.2 & 10.3 show the variation, with acetic acid as the solute, and Figs. 10.4 & 10.5, with phenol as the solute. The curves for the surface active agents are similar in shape and to avoid repetition in this part of the text only one is given here, Fig. 10.6. The others are given in Figs. E.1 to E.4 of Appendix E. The data of Harkins & Humphrey⁸⁵ for the interfacial tension between benzene and dilute aqueous acetic acid are in agreement with those obtained and are shown in Fig. E.5 of Appendix E. No literature values could be found for the interfacial tension of the system benzene-phenol-water.

10.3 Dynamic Interfacial Tension

All the values of interfacial tension referred to above were static equilibrium values. However, in all mass transfer processes the phases will not be in equilibrium and therefore some estimation of the dynamic (or non-equilibrium) interfacial tensions is necessary.

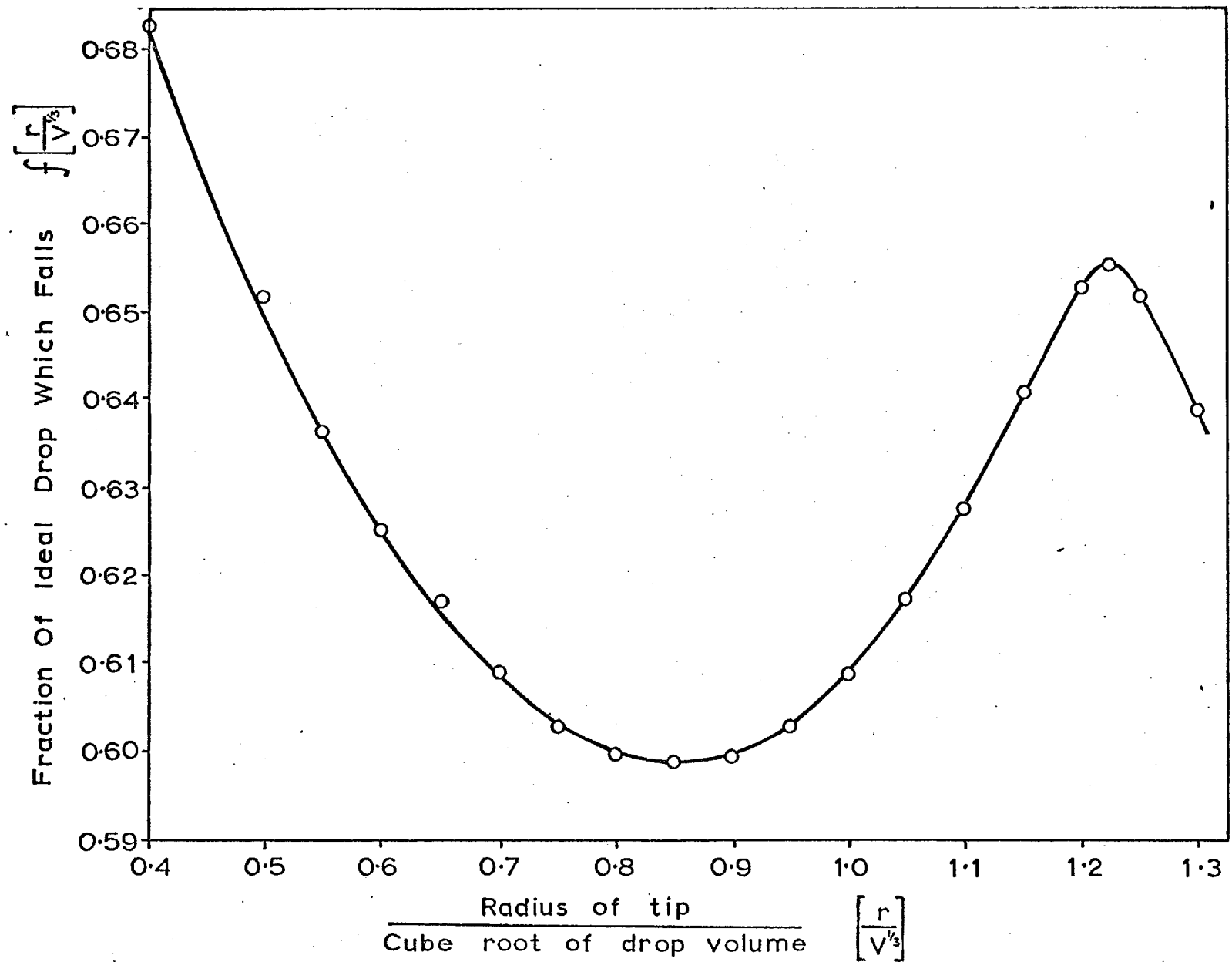


FIG.10.1:CORRECTION FACTOR USED IN EQUATION 10.1

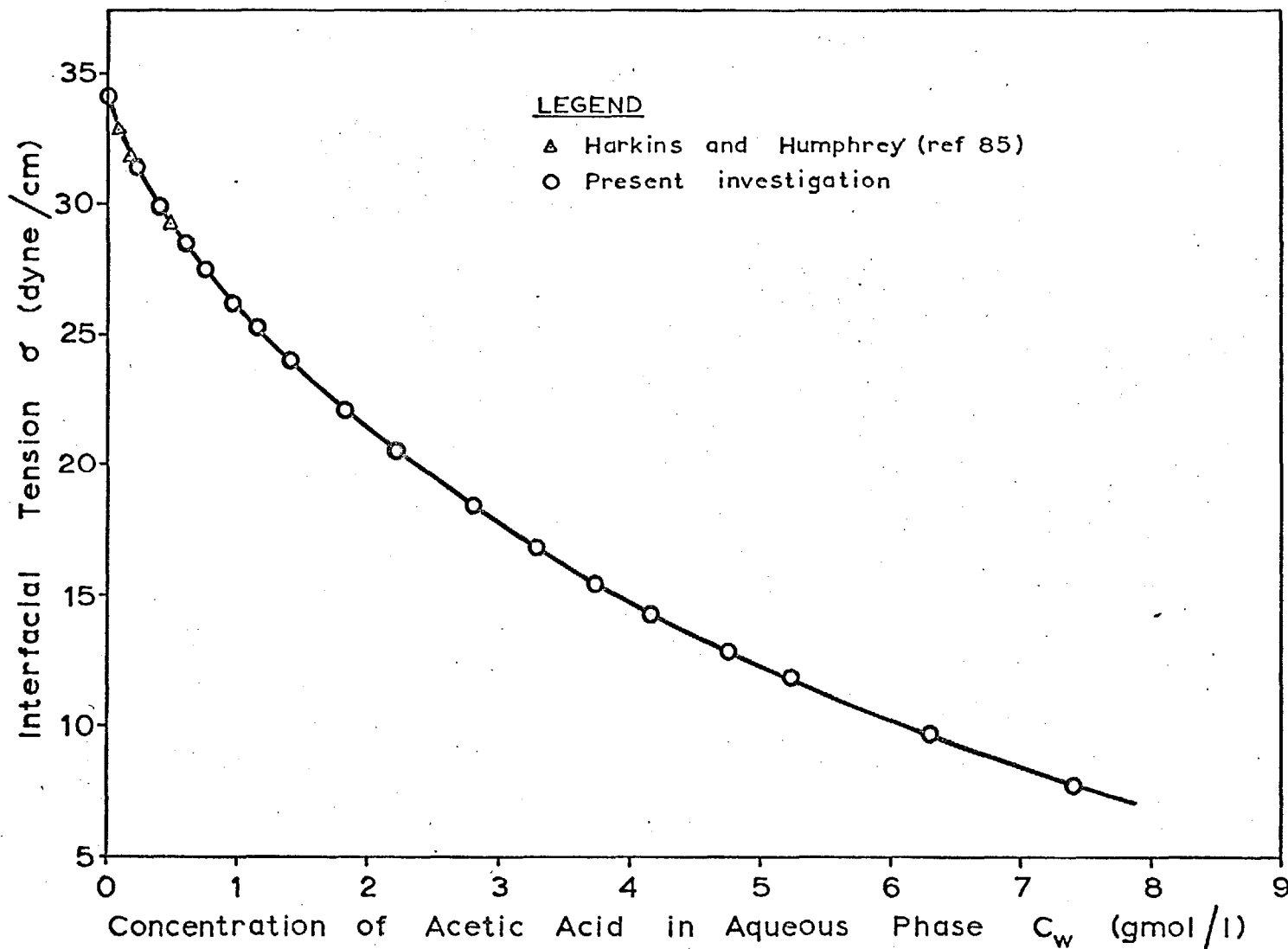


FIG.10.2: THE EQUILIBRIUM INTERFACIAL TENSION FOR THE BENZENE-
ACETIC ACID-WATER SYSTEM AT 25°C

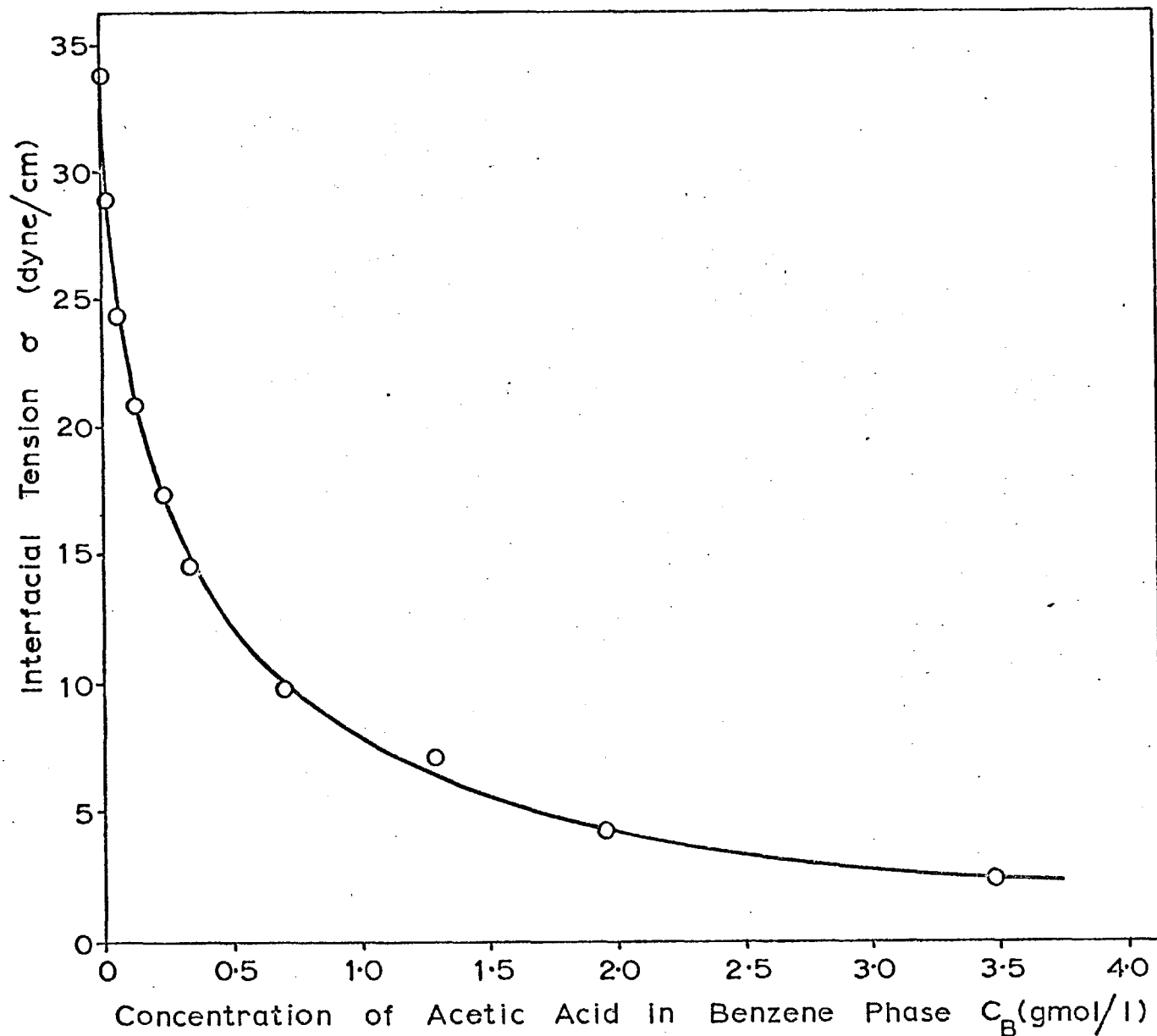


FIG.10.3:THE EQUILIBRIUM INTERFACIAL TENSION FOR THE BENZENE-
ACETIC ACID-WATER SYSTEM AT 25°C

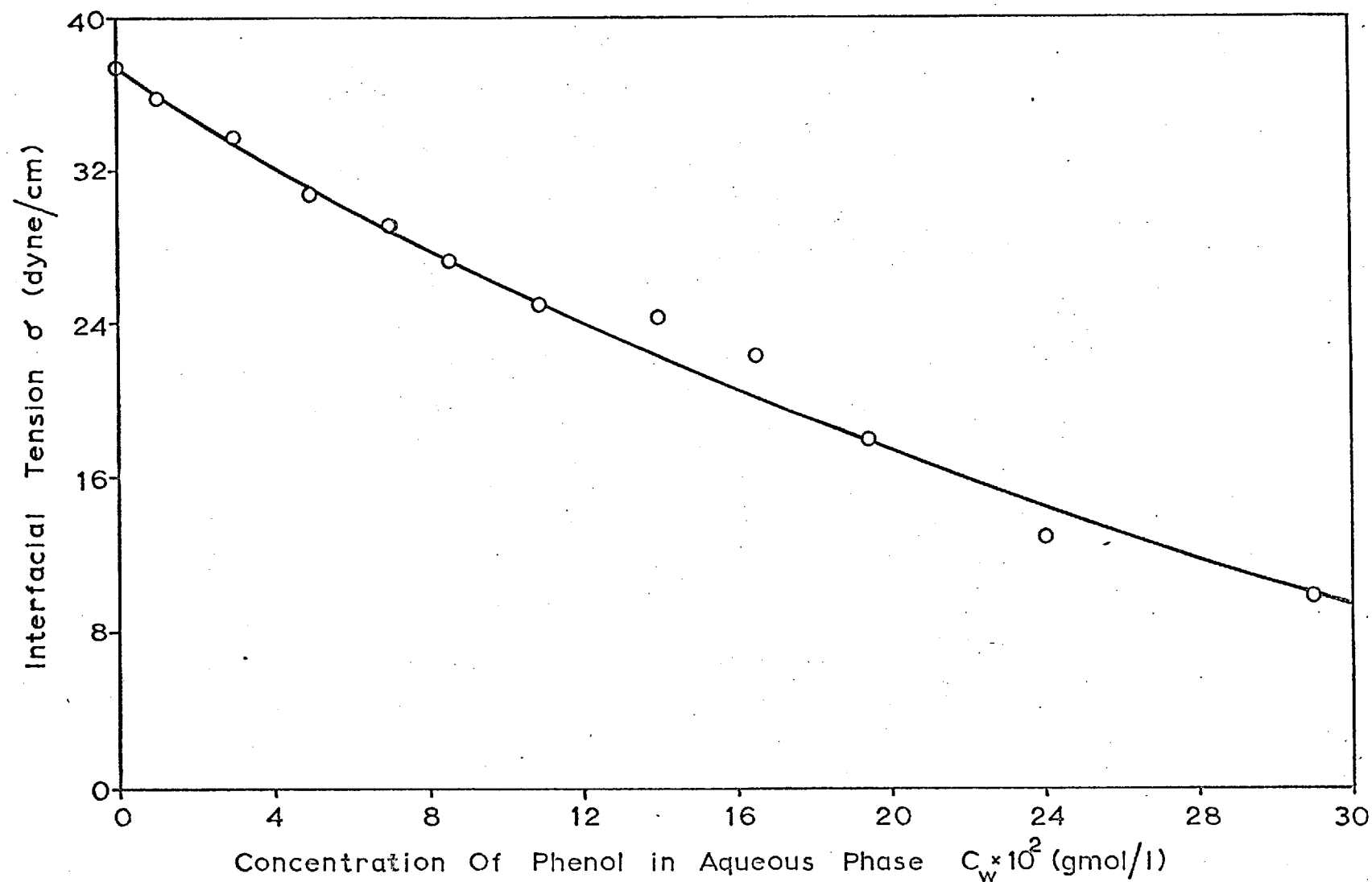


FIG.10.4:THE EQUILIBRIUM INTERFACIAL TENSION FOR THE BENZENE-
PHENOL-WATER SYSTEM AT 25°C

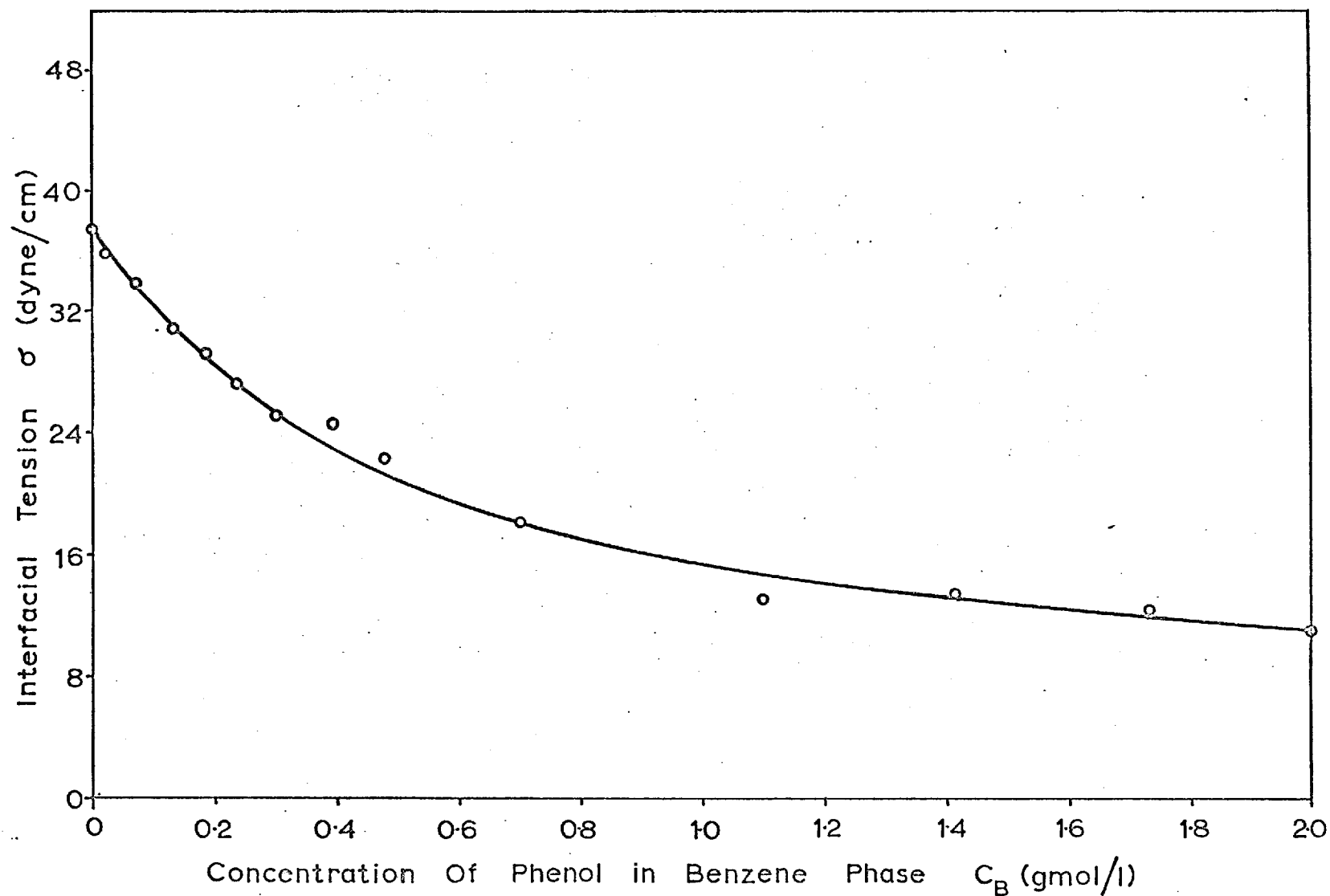


FIG.10.5:THE EQUILIBRIUM INTERFACIAL TENSION FOR THE BENZENE - PHENOL-WATER SYSTEM AT 25°C

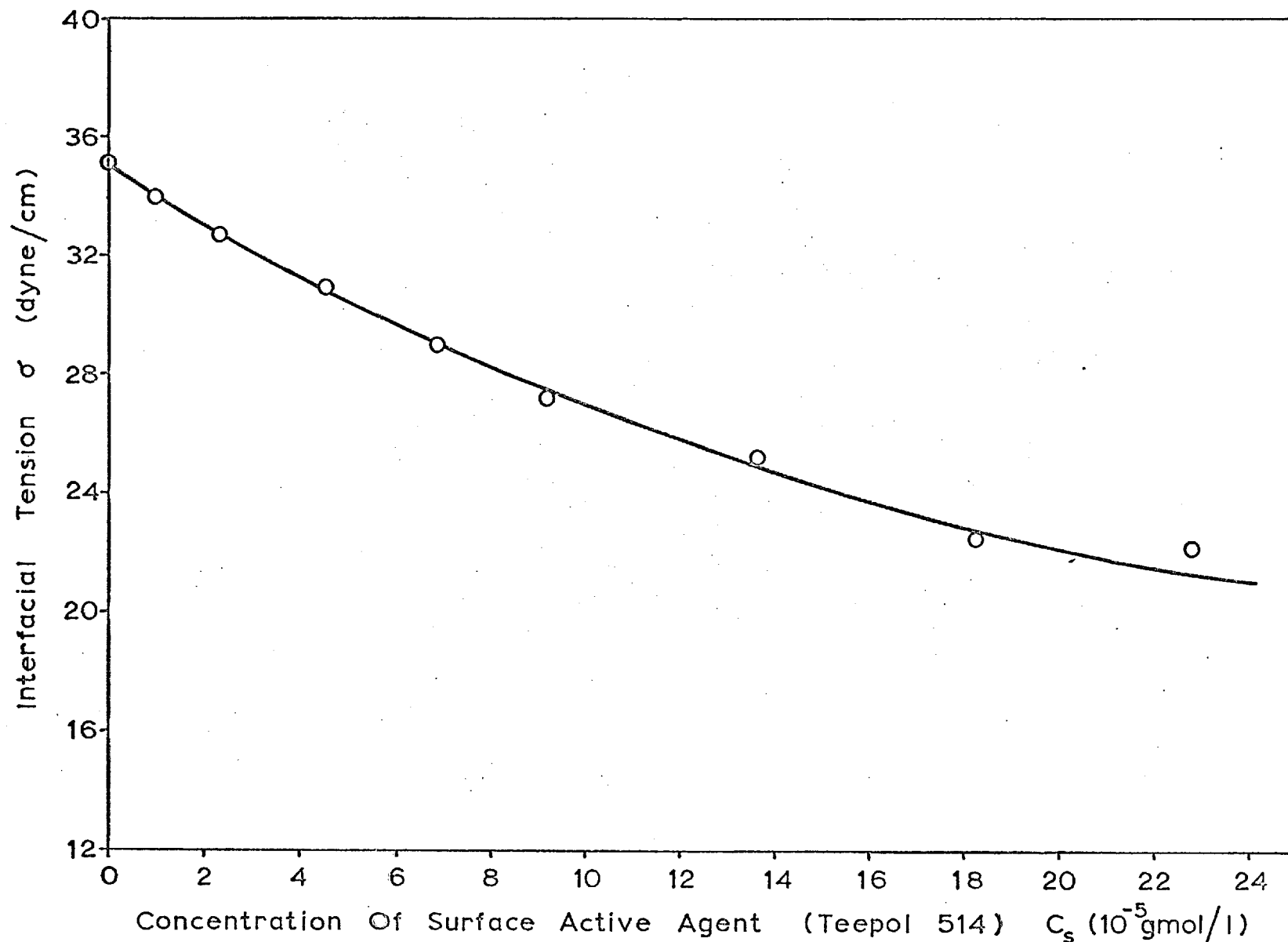


FIG.10.6: VARIATION OF INTERFACIAL TENSION WITH CONCENTRATION OF SURFACE ACTIVE AGENT TEEPOL 514 IN THE AQUEOUS PHASE

When two phases containing a solute are freshly contacted the interfacial tension will vary with time, because the interfacial excess of solute predicted by the Gibbs adsorption isotherm is not present in a fresh interface and needs time to build up. The value of this dynamic interfacial tension at the moment of first contact of the phases will be affected by the rate of increase of the surface excess of solute, by surface transport and by mass transfer(diffusion). Since there is no method of calculating this initial value of the dynamic interfacial tension it has been assumed that the adsorbed layer at the interface is formed instantaneously, or at least much more quickly than the mass transfer process. This implies that the interfacial tension at the moment of first contact between the phases is the static equilibrium interfacial tension corresponding to the bulk concentration of the phase from which the mass transfer takes place.

According to the penetration theory, at any time $t > 0$ the equilibrium concentrations at the interface are given by the equations

$$\sqrt{D_B} (C_B - C_{Bi}) = \sqrt{D_W} (C_{Wi} - C_W) \quad \dots \quad 10.2$$

where

D_B, D_W are the solute diffusivities in the benzene and aqueous phases respectively.

C_B, C_W are the bulk concentrations.

C_{Bi}, C_{Wi} are the equilibrium concentrations at the interfaces for the benzene and aqueous phases respectively.

If the distribution coefficient m between the phases is given by

the equation
$$C_{Bi} = m C_{Wi} + b$$

where b is a constant allowing for the possibility that a part of the

equilibrium curve is a straight line not passing through the origin, then

$$(C_{Wi} - C_W) = \sqrt{D_B/D_W} [C_B - (mC_{Wi} + b)]$$

$$\begin{aligned} \text{i.e.} \quad C_{Wi} &= \frac{C_W + C_B \sqrt{D_B/D_W} - b \sqrt{D_B/D_W}}{1 + m \sqrt{D_B/D_W}} \\ \text{and} \quad C_{Bi} &= \frac{C_W + C_B \sqrt{D_B/D_W} + b/m}{1/m + \sqrt{D_B/D_W}} \end{aligned} \quad \left. \vphantom{\begin{aligned} C_{Wi} \\ C_{Bi} \end{aligned}} \right\} \dots 10.3$$

The value of m in these equations is that corresponding to the interface concentration and hence these equations must be solved for C_{Wi} and C_{Bi} by trial and error.

Corresponding to the concentration at the interface there will be an equilibrium interfacial tension σ_i^* and hence an equilibrium value of the surface pressure $\pi_i^* (= \sigma_o - \sigma_i^*)$. The initial dynamic value of the interfacial tension is taken as the equilibrium interfacial tension corresponding to the concentration of the solute in the bulk of the benzene phase, σ_{Bb}^* , and hence the equilibrium surface pressure corresponding to this dynamic value will be $\pi_{Bb}^* (= \sigma_o - \sigma_{Bb}^*)$. The difference between these two values of the surface pressure is termed the "surface pressure difference" $\Delta\pi$, i.e.

$$\Delta\pi = \pi_{Bb}^* - \pi_i^* = \sigma_i^* - \sigma_{Bb}^*$$

For the transfer of solute in the opposite direction, i.e. from the aqueous continuous phase to the benzene droplet

$$\Delta\pi = \pi_{Wb}^* - \pi_i^* = \sigma_i^* - \sigma_{Wb}^*$$

where

$$\pi_{Wb}^* = (\sigma_o - \sigma_{Wb}^*), \quad \pi_i^* = (\sigma_o - \sigma_i^*)$$

and σ_{Wb}^* is the equilibrium interfacial tension corresponding to the solute concentration in the bulk of the aqueous phase, and σ_i^* is that corresponding to the interface concentration of solute.

For the system benzene-acetic acid-water at 20°C

$$D_B = 1.92 \times 10^{-5} \text{ cm}^2/\text{sec} \quad \text{Refs. 86,87.}$$

$$D_W = 0.88 \times 10^{-5} \text{ cm}^2/\text{sec} \quad \text{Refs. 88,89.}$$

giving

$$\sqrt{D_B/D_W} = \sqrt{1.92/0.88} = 1.48$$

For the system benzene-phenol-water at 20°C

$$D_B = 1.68 \times 10^{-5} \text{ cm}^2/\text{sec} \quad \text{Ref. 90.}$$

$$D_W = 0.84 \times 10^{-5} \text{ cm}^2/\text{sec} \quad \text{Ref. 91}$$

giving

$$\sqrt{D_B/D_W} = \sqrt{1.68/0.84} = 1.41$$

11. SURFACE COMPRESSIBILITY AND ITS DETERMINATION

11.1 Survey

It may be shown qualitatively with talc particles that the presence of a monolayer at a liquid-liquid interface greatly reduces the liquid movements at the interface. The monolayer restrains fresh liquid from being swept into the interface by eddies and movements within the bulk of the phase.

Consider a monolayer present at an interface between two immiscible solvents A and B, with the surface active solute molecules orientated as shown in Fig. 11.1. An eddy from within the bulk of solvent A causes local movement of surface active solute molecules from the interface, as shown, by partially clearing the surface at B and causing compression of the molecules at C and D. Consequently, owing to the high concentration of surface active solute molecules at C and D, a surface pressure difference $\Delta\pi$ will be set up which will tend to restore the equal distribution of molecules in the interface. This "back spreading" surface pressure gradient opposes and ultimately damps out the liquid movement caused by the eddy.

Quantitatively the variable concerned is the surface compressional modulus M given by equation 8.1, page 53

$$M = - A \frac{d(\Delta\pi)}{dA}$$

Since this back spreading surface pressure gradient opposes movement of the eddy at the interface, it will also oppose surface renewal and hence

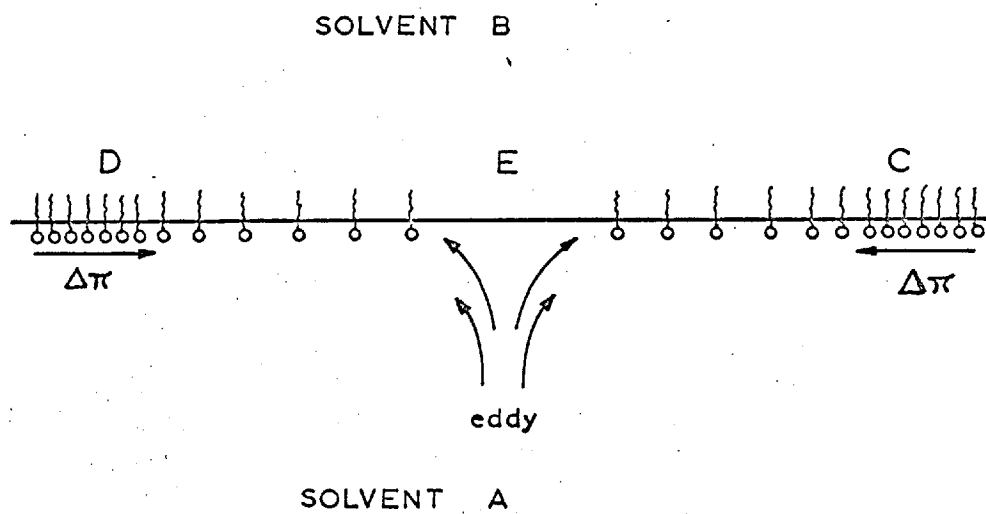


FIG. 11.1

the rate of mass transfer across the interface.

Davies & Mayers⁵⁰ have shown that for insoluble surface active agents - such as plasma albumen protein - the effect of these monolayers on the mass transfer rate across the interface in a stirred cell depends quantitatively on the surface compressional modulus M , and that this quantity correlates the effect of these monolayers on the overall mass transfer coefficient.

Our investigation has been made in an attempt to find the effect of the surface compressional modulus on the mass transfer rate for the case of soluble surface active agents, and more generally to extend it to solutes.

For a soluble surface active agent the surface compressibility cannot be measured experimentally, and it has been determined by calculation, both graphically and numerically.

11.2 Graphical Method of Determining Surface Compressibility

This method employs the Gibbs adsorption isotherm to calculate the value of A , the interfacial area available per molecule in the interface

$$\Gamma_s = - \frac{N}{RT} \frac{d\sigma}{d(\ln a)} \quad \dots \quad 11.1$$

where

Γ_s = the interfacial excess of solute, i.e. the number of solute molecules in the interfacial zone less the number that would be there if the bulk concentration were to extend unchanged up to the interface.

- R = the universal gas constant, 8.314×10^7 erg/deg/mole
 T = absolute temperature (here 25°C , i.e. 298.16°A)
 N = the Avogadro Number, 6.023×10^{23} molecules/mole.
 σ = the interfacial tension
 a = the activity of the solute

Assuming activity to be proportional to concentration, which is valid for dilute solutions, and substituting the numerical values of R , T and N in equation 11.1, the following equation was used for the calculation of Γ_s

$$\Gamma_s = 2.42 \times 10^{13} C \frac{d\sigma}{dC} \text{ molecules/cm}^2 \quad \dots \quad 11.2$$

where the units of C and σ are moles/litre and dynes/cm respectively.

Hence, by measuring $d\sigma/dC$ from the plot of σ vs C , the surface excess Γ_s was found.

The contribution of the bulk concentration Γ_b was given by

$$\begin{aligned} \Gamma_b &= N d' C \\ &= 6.023 \times 10^{20} d' C \text{ molecules/cm}^2 \quad \dots \quad 11.3 \end{aligned}$$

where d' is the diameter of a molecule in cm and the units of C are moles/litre.

The diameter of the molecule was given by

$$d' = \sqrt[3]{\frac{\text{molar volume}}{N}} \quad \dots \quad 11.4$$

The molar volumes of acetic acid and phenol were calculated using the Kopp rule⁹², the atomic volumes⁹³ of each constituent element in the

molecule being added together. For phenol and acetic acid the molar volumes were calculated to be as follows

phenol ... 103.4 cm³ acetic acid ... 63.8 cm³

which gave in turn values for the diameters of the molecules

phenol ... 5.56 x 10⁻⁸ cm acetic acid ... 4.74 x 10⁻⁸ cm

comparing favourably with the values of the collision diameters given in reference⁹⁴.

Thus, the surface concentration of solute molecules was found from the sum of Γ_s and Γ_b with the reciprocal of this giving the surface area available per molecule, A , i.e.

$$A = 1/(\Gamma_s + \Gamma_b) \quad \dots \quad 11.5$$

The surface pressure^{difference} $\Delta\pi$ was then plotted vs A and the surface compressional modulus calculated as $-A(d\Delta\pi/dA)$.

For the solutes acetic acid and phenol, M was calculated using interfacial concentrations, and in this case $\Delta\pi$ was the difference between the interfacial tension corresponding to the concentration at the interface and that corresponding to the concentration in the bulk of the phase.

For the surface active agents the surface pressure was taken as the lowering of the interfacial tension caused by their presence, and the contribution due to the bulk Γ_b was neglected since it was negligible compared with Γ_s .

However, this graphical method is susceptible to large errors involved in drawing tangents to the σ vs C and $\Delta\pi$ vs A curves, to evaluate $d\sigma/dC$ and $d\Delta\pi/dA$ respectively. In order to eliminate these errors an attempt was made to find an equation which would represent the variation of σ with C whence the surface compressibility could be determined numerically

11.3 Numerical Method of Determining Surface Compressibility

Suppose the relationship between σ and C is of the form

$$\sigma = \sigma_0 - \alpha C^n \quad \dots \quad 11.6$$

where σ_0 is the interfacial tension in the absence of surface active agent or solute, and α, n are constants. Thus

$$\sigma_0 - \sigma = \pi = \alpha C_s^n \quad \dots \quad 11.7$$

From equation 11.1

$$\begin{aligned} T_s &= \frac{N}{RT} \frac{d\sigma}{d(\ln a)} \\ &= \frac{N}{RT} C \frac{d\sigma}{dC} \quad \dots \quad 11.8 \end{aligned}$$

From equation 11.6

$$\frac{d\sigma}{dC} = -n \alpha C^{n-1} \quad \dots \quad 11.9$$

Therefore,

$$\begin{aligned} T_s &= -\frac{N}{RT} C(-n\alpha C^{n-1}) \\ &= \frac{N}{RT} n\alpha C^n \quad \dots \quad 11.10 \end{aligned}$$

There are two possible cases, depending upon the magnitudes of T_b and T_s with respect to each other.

Case (i) - T_b negligible compared with T_s

Then equation 11.5 reduces to

$$\begin{aligned} A &= 1/T_s \\ &= RT/Nn\alpha C^n \end{aligned} \quad \dots \quad 11.11$$

Now

$$\begin{aligned} M &= -A(d\pi/dA) \\ &= -A(d\pi/dC)(dC/dA) \end{aligned}$$

From equation 11.7

$$d\pi/dC = n\alpha C^{n-1}$$

and from equation 11.11

$$dA/dC = -RT/N\alpha C^{n+1}$$

$$\therefore M = \frac{RT}{Nn\alpha C^n} \cdot n\alpha C^{n-1} \cdot \frac{N\alpha C^{n+1}}{RT}$$

i.e.

$$\underline{\underline{M = \alpha C^n}} \quad \dots \quad 11.12$$

Case (ii) - T_b not negligible compared with T_s

i.e.

$$A = 1/(T_s + T_b)$$

Now

$$\begin{aligned} T_b &= N d' C \\ &= a C \quad \text{say where } a = N.d' \end{aligned}$$

and

$$\begin{aligned} T_s &= N/RT(n\alpha C^n) \\ &= b C^n \quad \text{say where } b = Nn\alpha/RT \end{aligned}$$

$$\therefore A = 1/(bC^n + aC) \quad \dots \quad 11.13$$

$$\therefore dA/dC = -(nbC^{n-1} + a)/(bC^n + aC)^2$$

$$\therefore M = \left[\frac{1}{bC^n + aC} \right] n\alpha C^{n-1} \left[\frac{(bC^n + aC)^2}{nbC^{n-1} + a} \right]$$

$$\text{i.e.} \quad M = n\alpha C^n \left[\frac{bC^{n-1} + a}{nbC^{n-1} + a} \right] \quad \dots \quad 11.16$$

$$\text{Now} \quad b = (N/RT) n\alpha = 2.42 \cdot 10^{13} n\alpha$$

$$\text{and} \quad a = N d' = 6.023 \cdot 10^{20} d' \quad \dots$$

if C is in moles/litre

$$\therefore M = n\alpha C^n \left[\frac{n\alpha C^{n-1} + 2.49 \cdot 10^{10} d'}{n^2 \alpha C^{n-1} + 2.49 \cdot 10^{10} d'} \right] \quad \dots \quad 11.15$$

Initially it was supposed that the relationship between σ and C was of the form

$$(\sigma_\theta - \sigma) = \pi = \alpha C^n \quad \dots \quad 11.7$$

$$\text{Therefore} \quad \log \pi = \log \alpha + n \log C \quad \dots \quad 11.16$$

and if this relationship holds the plot of $\log \pi$ vs $\log C$ should be a straight line of slope n and giving an intercept of value $\log \alpha$.

For all the surface active agents and for the transfer of phenol from water to benzene, such a plot gives connected straight lines of different slope, indicating that the relationship of equation 11.16 holds, but with different values of n and α for each of the two ranges of concentration in which the straight lines occur (Figs. G.9 to G.14 of Appendix G).

For the transfer of acetic acid and phenol from benzene to water equation 11.16 does not hold and in these cases a different relationship between σ and C was found. Here the plot of π vs $\log C$ was found to give two straight connected lines of different slope for the two ranges of concentration (Figs. G.5 to G.8 of Appendix G). This indicates that the relationship between π and C is of the form

$$\begin{aligned} (\sigma_{Bi} - \sigma_{Bb}) &= \pi = -n_1 \log C + \alpha_1 \quad \text{for range 1} \\ (\sigma_{Bi} - \sigma_{Bb}) &= \pi = -n_2 \log C + \alpha_2 \quad \text{for range 2} \end{aligned} \quad \dots \quad 11.17$$

or more generally

$$\pi = -n \log C + \alpha \quad \dots \quad 11.18$$

Hence an expression for M can be evaluated as follows:

From equation 11.18

$$\begin{aligned} \frac{d\sigma}{dC} &= -n \frac{d\sigma}{dC} (\log C) \\ &= -\frac{n}{C} \end{aligned} \quad \dots \quad 11.19$$

$\therefore$ from equation 11.8

$$\begin{aligned} T_s &= -\frac{N}{RT} C \frac{d\sigma}{dC} \\ &= Nn/RT \end{aligned} \quad \dots \quad 11.20$$

From equation 11.3

$$T_b = N d' C$$

$$\therefore A = 1/(T_s + T_b) = \frac{1}{\frac{Nn}{RT} + Nd'C} = 1/(a + bC) \quad \dots \quad 11.21$$

$$\begin{aligned} \text{where} \quad a &= Nn/RT = 2.42 \cdot 10^{13} n \\ b &= N d' = 6.023 \cdot 10^{23} d' \end{aligned}$$

$$\text{Now} \quad M = -A(d\pi/dA) = -A/d\pi/dC)(dC/dA)$$

and, from 11.21

$$dC/dA = -(a + bC)^2/b$$

$$\therefore M = -n(a + bC)/bC \quad \dots \quad 11.22$$

$$= - \frac{n(2.42 \cdot 10^{13} n + 6.023 \cdot 10^{23} d' C)}{6.023 \cdot 10^{23} d' C}$$

$$= - \frac{0.4n^2 + 10^{10} n d' C}{10^{10} d' C} \quad \dots \quad 11.23$$

For acetic acid, $d' = 4.74 \cdot 10^{-8} \text{ cm}$

$$\text{thus} \quad M = - \frac{0.846 \cdot 10^{-3} n^2}{C} + \frac{nC}{C} \quad \dots \quad 11.24$$

For phenol, $d' = 5.56 \cdot 10^{-8} \text{ cm.}$

$$\text{thus} \quad M = - \frac{0.721 \cdot 10^{-3} n^2}{C} + \frac{nC}{C} \quad \dots \quad 11.25$$

Davies & Rideal⁷⁶ have reviewed the literature on the various relationships between π and C . Using the Küster⁹⁵ isotherm and the Gibb's equation⁹⁶ they have revised Szyszkowski's⁹⁷ $\pi - C$ relation to apply to charged films at the oil-water interface, and give the relationship

$$\log \pi = \frac{2}{3} \log C + \log (3k'TK) \quad \dots \quad 11.26$$

where k' is the Boltzmann constant, T the absolute temperature and

and K is a constant. This equation has been tested^{98,99} using salt as the electrolyte and a straight line was obtained, of slope $2/3$ and giving a value of 3.14 for the constant, compared with the calculated value of 3.04.

For the transfer of acetic acid and of phenol from benzene to water the relationship obtained between π and C was similar in form to that given by Szyszkowski⁹⁷. For the transfer of phenol from water to benzene, and for all the surface active agents used, the relationship between π and C was of the same form as that given in equation 11.26 above. In both cases the slope of the straight lines and the values of the constant depended on the concentration range in which one operated.

11.4 Results

The surface compressibility has been evaluated both graphically and numerically. The latter method has been taken as giving the more correct values and it is these that have been used. The results for both methods are given in detail in Tables I & II of Appendices F and G.

For the transfer of acetic acid from benzene to water Figs. 11.2, 11.3 and 11.4 indicate the variation of M^{-1} (evaluated numerically) with the concentration of acetic acid in the benzene phase at the interface, and Figs. F.1., F.2, and F.3 of Appendix F give the π - A plots which were used for the graphical evaluation

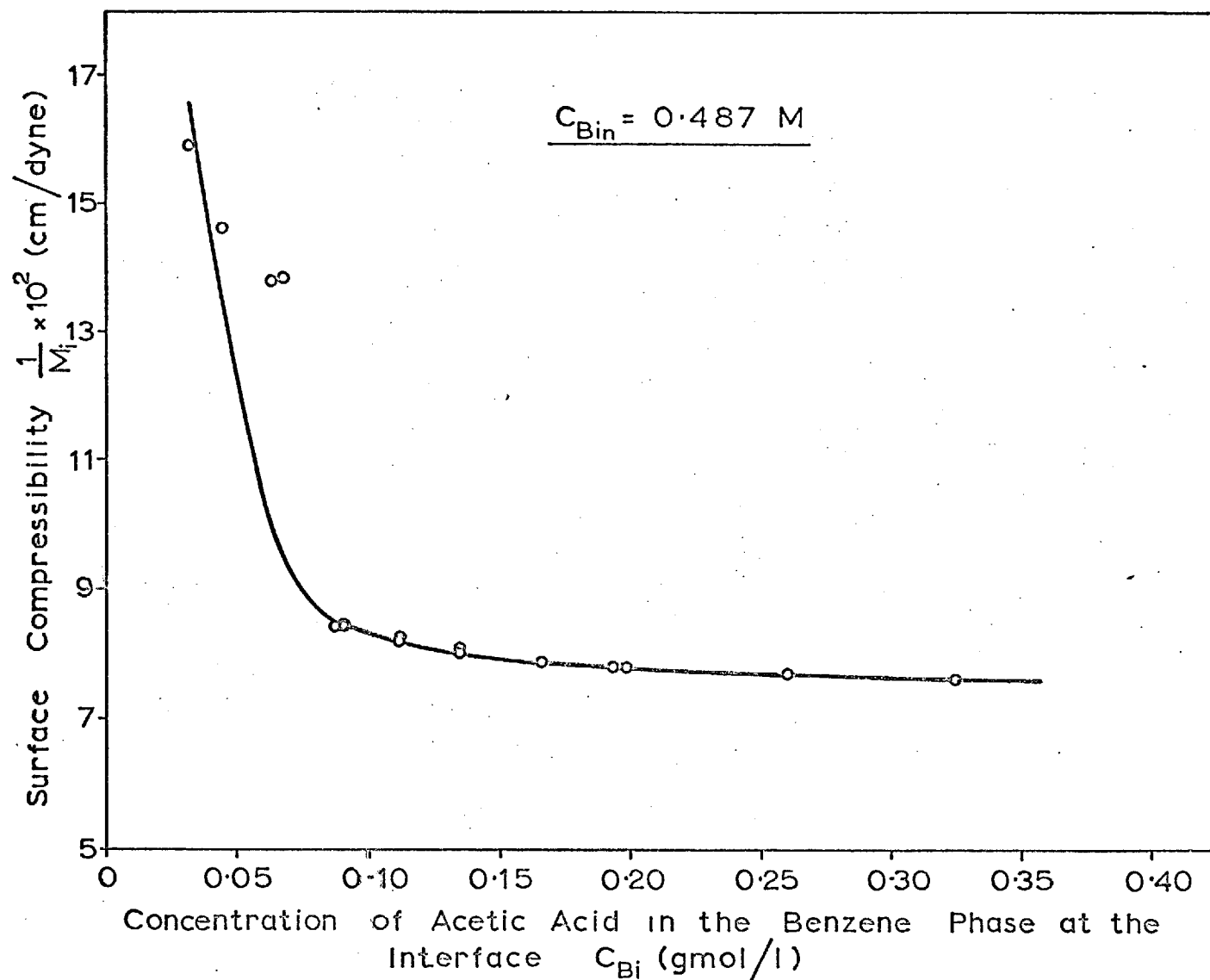


FIG.11.2: SURFACE COMPRESSIBILITY AS A FUNCTION OF THE CONCENTRATION OF ACETIC ACID IN THE BENZENE PHASE AT THE INTERFACE

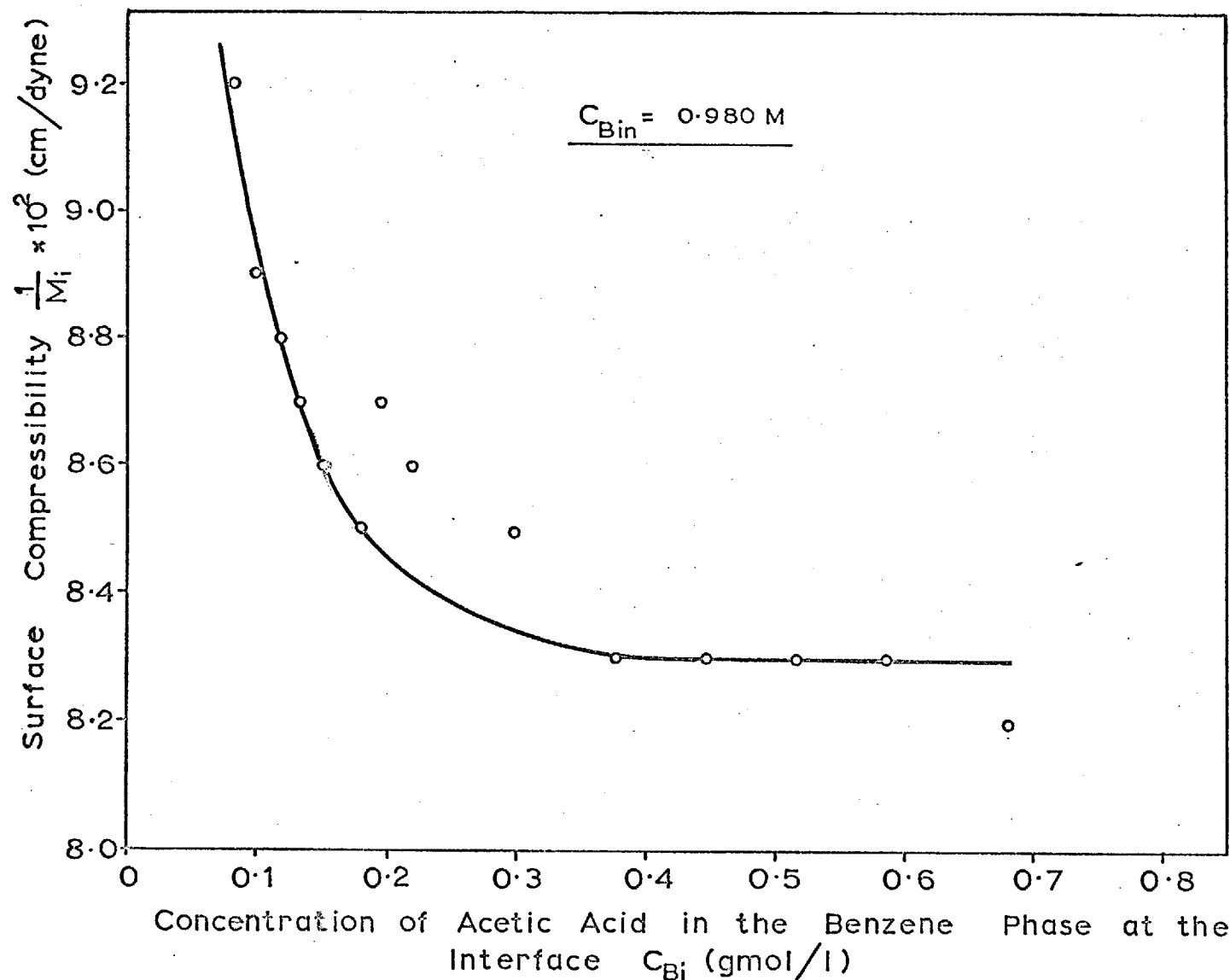


FIG.11.3: SURFACE COMPRESSIBILITY AS A FUNCTION OF THE CONCENTRATION OF ACETIC ACID IN THE BENZENE PHASE AT THE INTERFACE

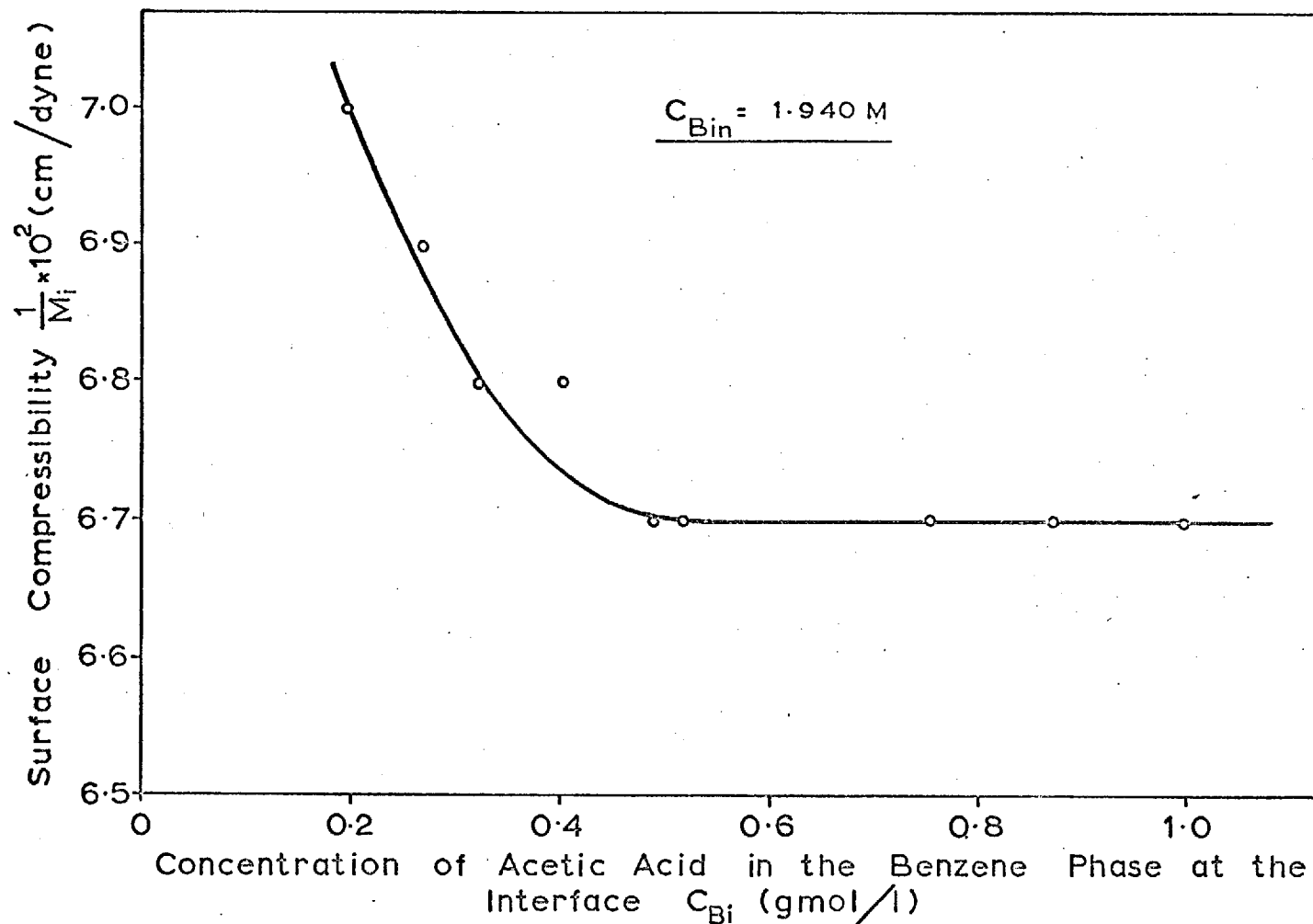


FIG. 11.4: SURFACE COMPRESSIBILITY AS A FUNCTION OF THE CONCENTRATION OF ACETIC ACID IN THE BENZENE PHASE AT THE INTERFACE

of M^{-1} . Fig. 11.5 shows the dependence for the transfer of phenol from water to benzene with the corresponding π - A plot given in Fig. F.4 of Appendix F.

The variation of M^{-1} (evaluated numerically) with concentration of surface active agent, C_s , is similar for all surface active agents. Hence only one curve is shown here, Fig. 11.6, the rest are given in Figs. G.1, G.2, G.3 and G.4 of Appendix G. The π - A plots for all surface active agents are given in Figs. F.5 to F.9 of Appendix F.

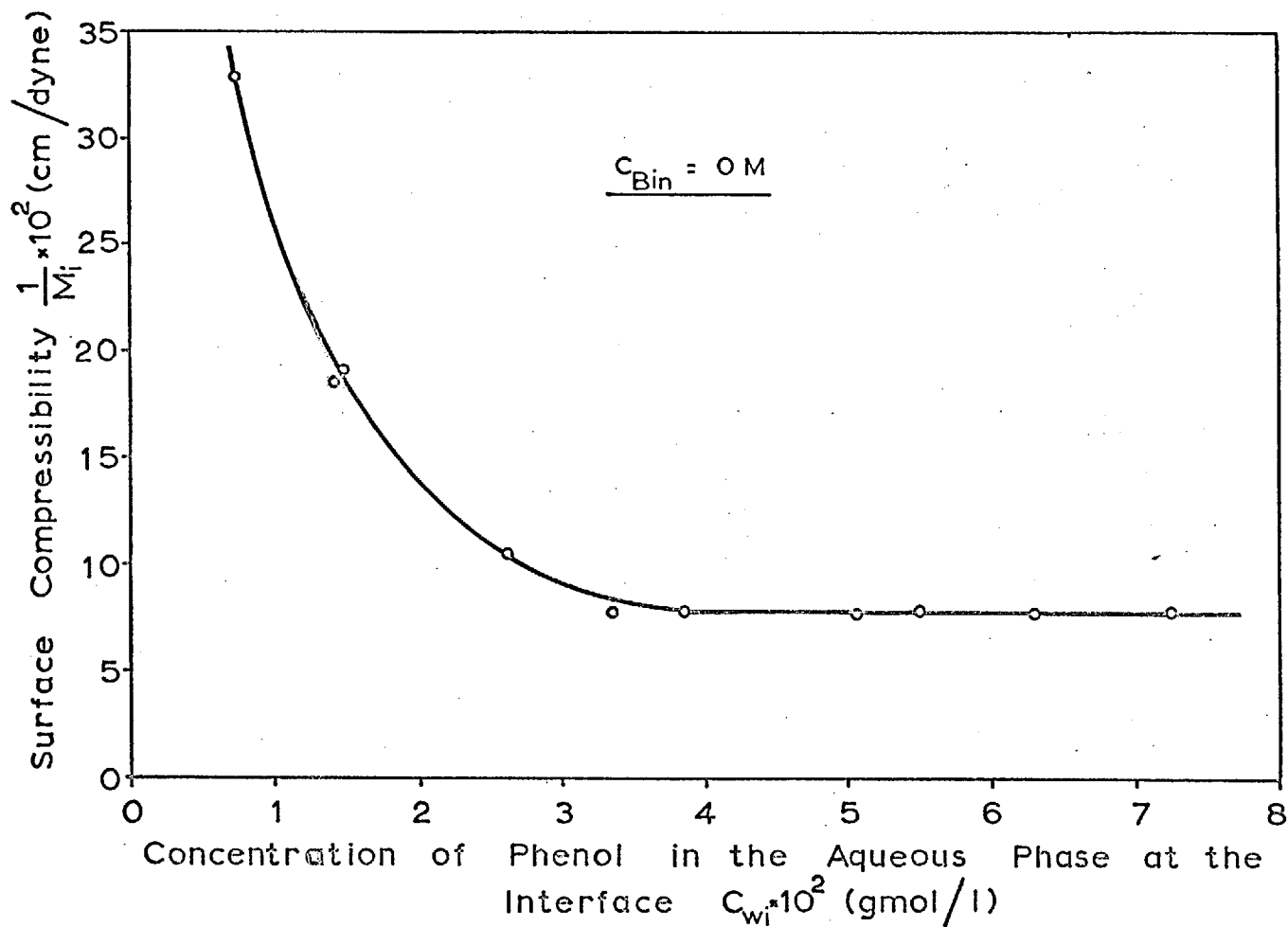


FIG.11.5: SURFACE COMPRESSIBILITY AS A FUNCTION OF THE CONCENTRATION OF PHENOL IN THE AQUEOUS PHASE AT THE INTERFACE

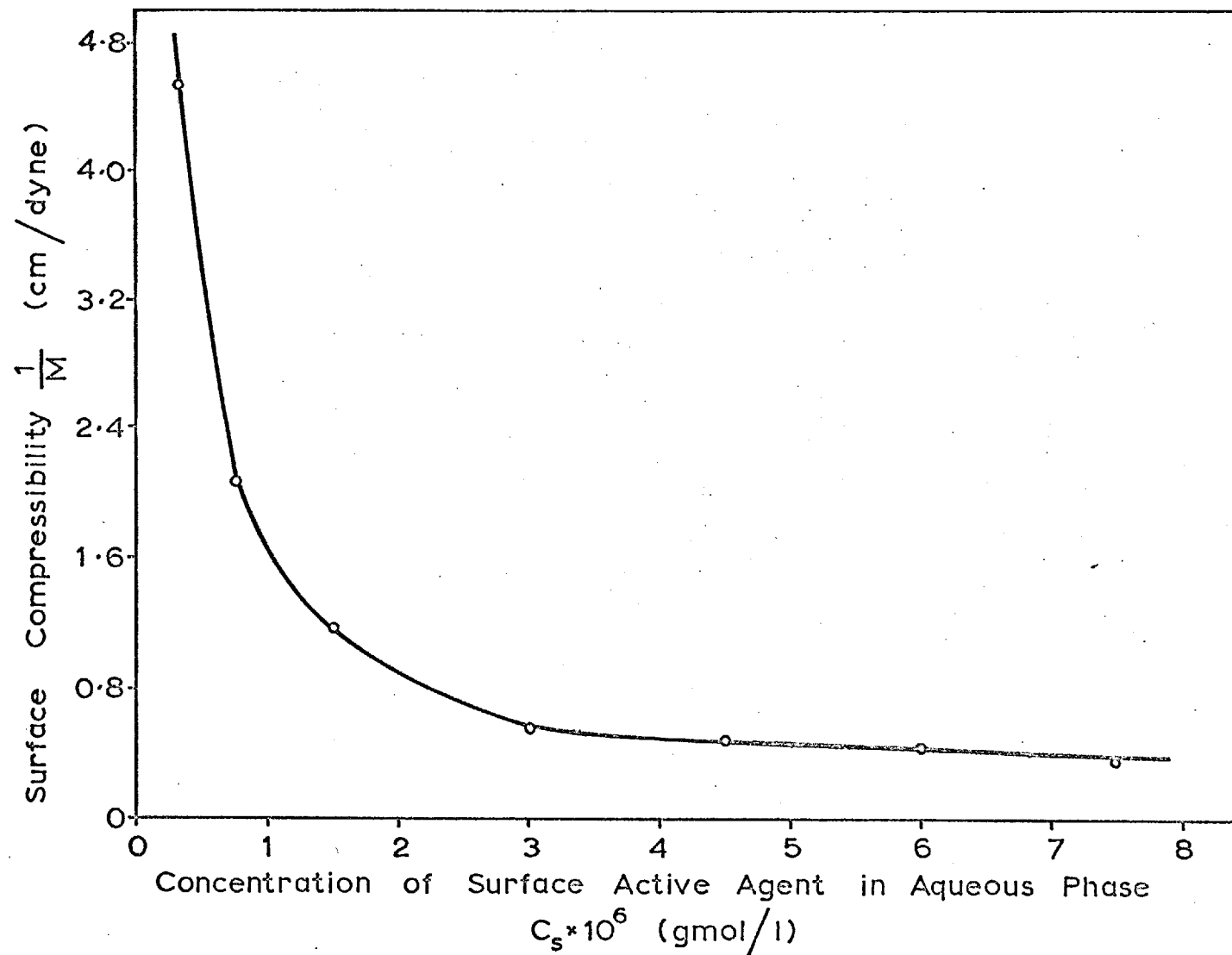


FIG.11.6: SURFACE COMPRESSIBILITY AS A FUNCTION OF THE CONCENTRATION OF SURFACE ACTIVE AGENT SODIUM LAURYL SULPHATE IN THE AQUEOUS PHASE

12. EVALUATION OF EXPERIMENTAL RESULTS

12.1 Method

All the experimentally determined mass transfer coefficients were calculated on the basis of a constant (initial) driving force, from the equation

$$\begin{aligned} K_{od} &= Q / \bar{A} T_p (C_{B_{in}} - m C_w) \\ &= V (C_{B_{in}} - C_{B_{out}}) / \bar{A} T_p (C_{B_{in}} - m C_w) \\ &= VE / \bar{A} T_p \end{aligned} \quad \dots \quad 12.1$$

where

- K_{od} = overall mass transfer coefficient
- Q = total quantity of solute transferred
- $C_{B_{in}}$ = inlet concentration of solute in the benzene phase
- $C_{B_{out}}$ = outlet concentration of solute in the benzene phase
- C_w = concentration of solute in the aqueous phase
- V = the drop volume
- $\bar{A}$ = the time mean area of one cycle
- E = the fractional extraction
- T_p = the time of one cycle

Equation 12.1 was used to calculate all mass transfer coefficients which are given in Tables I & II of Appendix B.

For direct comparison with the theoretical mass transfer coefficient the above value must be calculated on the basis of a logarithmic mean driving force, i.e. by substituting for E , the

fractional extraction,

$$E = \log \frac{(C_{B_{in}} - mC_w)}{(C_{B_{out}} - mC_w)}$$

Some recalculated values are given in Chapter 14.

12.2 Specimen Calculation

Run 20: Here $C_w = 0.604M$ $C_{B_{in}} = 0.980M$ $C_{B_{out}} = 0.819M$

From the equilibrium curve, Fig. 7.1 (see text p. 50) the value of mC_w corresponding to $C_w = 0.604M$ is $0.020M$. Hence E is given by

$$\begin{aligned} E &= \frac{C_{B_{in}} - C_{B_{out}}}{C_{B_{in}} - mC_w} \\ &= \frac{.980 - .819}{.980 - .020} \\ &= \frac{0.161}{0.960} \\ &= \underline{\underline{0.168}} \end{aligned}$$

The time T_p for one complete revolution was 3.50 sec.

V and $\bar{A}$ were constant (for all runs) at 0.040 cm^3 and 0.1612 cm^2 respectively. Thus

$$\begin{aligned} K_{od} &= VE / \bar{A}T_p \\ &= \frac{.040 \times 0.168}{.1612 \times 3.50} \\ &= \underline{\underline{0.0118 \text{ cm/sec.}}} \end{aligned}$$

12.3 Errors in the Mass Transfer Coefficient

A. Drop Volume

With the pump micrometer position at 2.00, repeated determinations of the volume of liquid delivered by the pump gave variations of the order of 0.5%. Thus, the error in drop volume is estimated as not exceeding 1%.

B. Pump Revolution Time

Using a stop-watch the time for 20 revolutions of the pump was measured to within ± 0.1 sec. Hence the possible error here is not more than 1%.

C. Concentration

Although the usual error involved in the mean concentration obtained from seven consecutive readings was estimated to be not greater than 1%, at low values of fractional extraction this is greatly increased and has been estimated to be as much as 8%. Therefore, allowing for this fact, an error of 5% is estimated as most usual.

D. Time Mean Area

Errors are likely to occur in the value of the time mean area, owing to the fact that the interface of the withdrawn drop might not always lie in the plane of the nozzle tip.

Let v be the volume between the plane of the nozzle tip and the interface. Then if V is the volume of the drop and e' the

error in the area of the drop, e' is given approximately by

$$\begin{aligned}
 e' &= \frac{v^{2/3} - (v - v)^{2/3}}{v^{2/3}} \\
 &= 1 - (1 - \frac{v}{V})^{2/3} \\
 &= 1 - (1 - \frac{2v}{3V}) \\
 &= 2v/3V \quad \dots \quad 13.2
 \end{aligned}$$

Now the drop exists on the end of the nozzle for only 0.346 of the time of one pump revolution, hence the error in the time mean area is given approximately by

$$\begin{aligned}
 e &= \frac{2}{3} \times 0.346 \times \frac{v}{V} \\
 &= 0.23 \frac{v}{V} \quad \dots \quad 13.3
 \end{aligned}$$

v/V is unlikely to exceed $1/8$, hence the error

$$\begin{aligned}
 e &= 0.23/8 \\
 &= \underline{\underline{2.88\%}}
 \end{aligned}$$

The error in $\bar{A}$ is therefore less than 3%

E. Total Error

Drop Volume	...	...	1%
Time	...	...	1%
Concentration	...	...	5%
$\bar{A}$	...	...	3%
			<u>10%</u>

Therefore experimental values as defined by equation 13.1 are concluded to be within $\pm 10\%$ of the true value.

13. CORRELATION OF RESULTS.

A. Absence of Surface Active Agents.

Investigations were conducted for the systems benzene-acetic acid-water and benzene-phenol-water, with the direction of transfer from the benzene to the aqueous continuous phase. In addition, the latter system was investigated with the direction of transfer reversed, that is to say from the aqueous continuous phase to the benzene droplet.

The inlet concentration of solute in the benzene phase was kept constant and the concentration of solute in the aqueous phase varied, thus varying the driving force and the interfacial properties.

13.1 Correlation in Terms of Changes in Concentration.

The results for the systems benzene-acetic acid-water and benzene-phenol-water, with the direction of transfer from the benzene to the aqueous phase (Table I of Appendix B), and the latter system with the direction of transfer reversed (Table I, Appendix B, Runs 144-153), indicated that the mass transfer coefficient depended on the concentration in the aqueous phase. Fig. 13.1 shows this dependence for acetic acid inlet concentrations in the benzene phase of 0.487 M , 0.980 M , and 1.940 M , and Fig. 13.2 that for an inlet phenol concentration in the benzene phase of 1.78 M , both with the direction of transfer from the benzene to the aqueous phase. Fig. 13.3 shows the dependence for an inlet phenol concentration of 0.0 M , with the direction of transfer reversed.

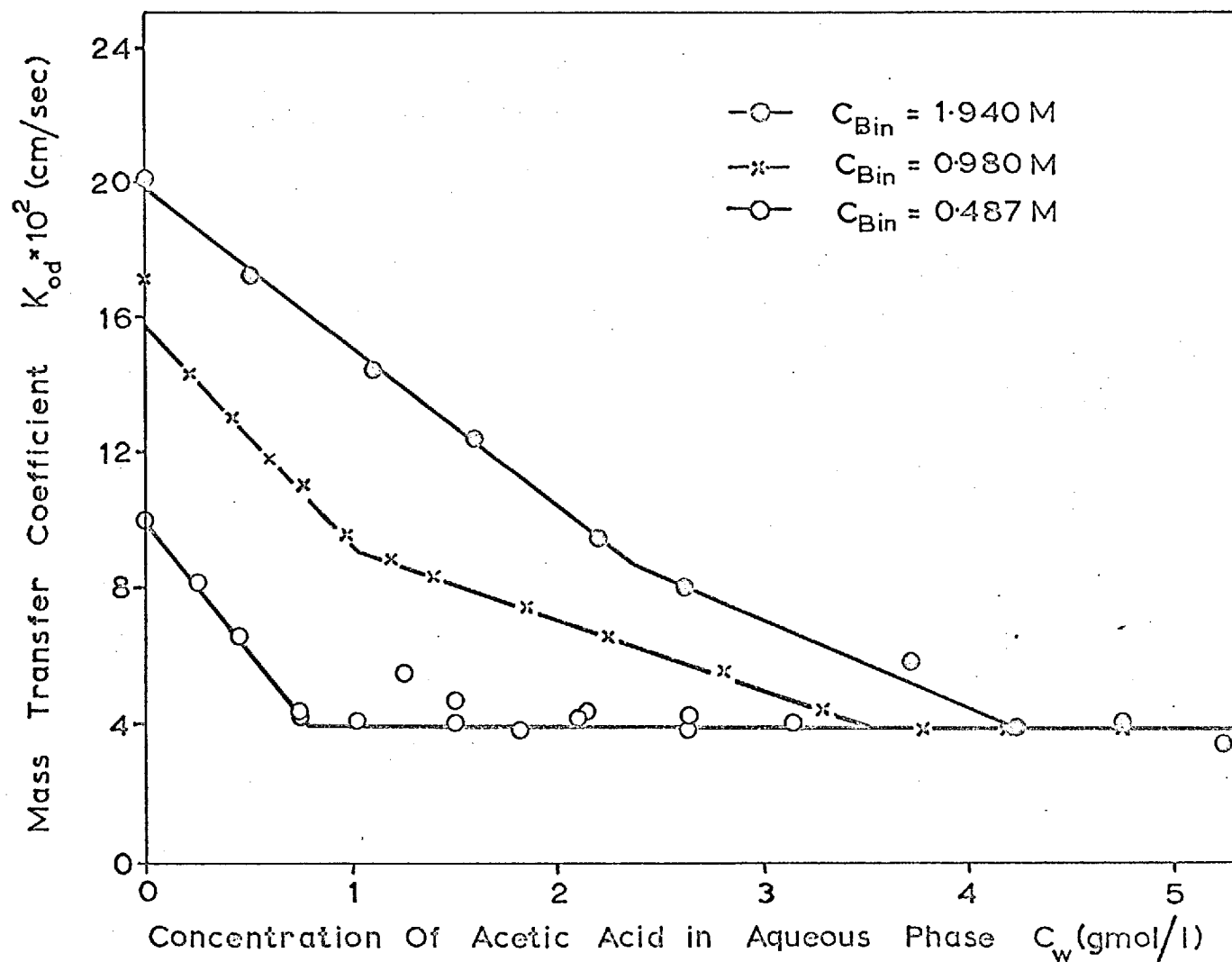


FIG. 13.1. MASS TRANSFER COEFFICIENTS AS A FUNCTION OF CONCENTRATION

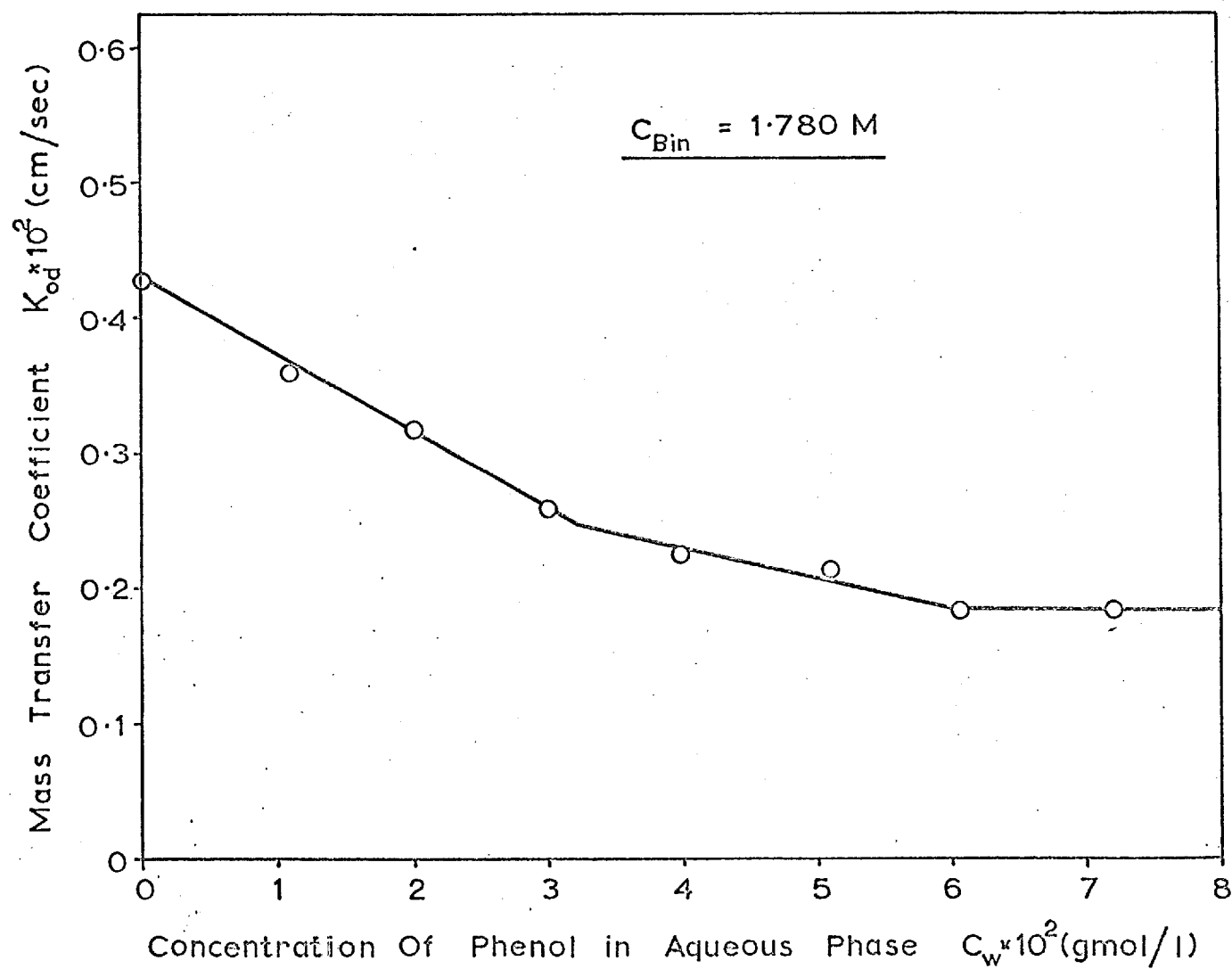


FIG. 13.2 : MASS TRANSFER COEFFICIENTS AS A FUNCTION OF CONCENTRATION

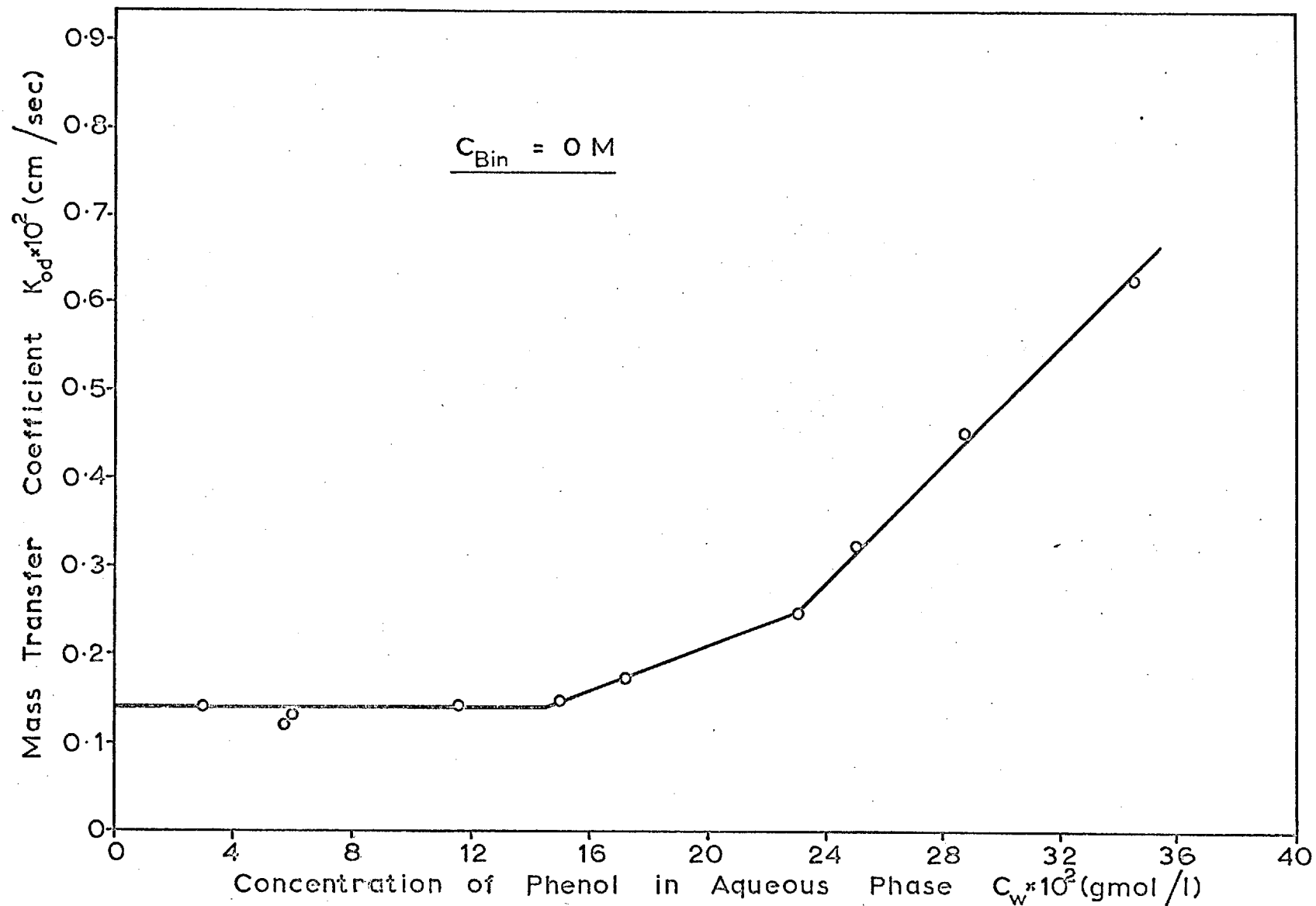


FIG. 13.3: MASS TRANSFER COEFFICIENTS AS A FUNCTION OF CONCENTRATION

In all systems the three regions of mass transfer are clearly indicated and they were confirmed by visual observation of the interface during each run. Fig. 13.1 indicates that as the solute concentration in the aqueous phase was increased so the mass transfer rate decreased until a critical concentration was reached - which differed for each benzene phase inlet concentration. Further increases in the aqueous phase concentration did not affect the value of the mass transfer coefficient, which remained constant at 0.004 cm/sec for the benzene-acetic acid-water system. This constant value of the mass transfer coefficient is termed the "diffusional" value, since the transfer over this concentration range is steady and diffusional in character.

The variation for the benzene-phenol-water system, Fig. 13.2, is very similar to the above system, the mass transfer coefficient decreasing with increasing solute concentration in the aqueous phase. Owing to the unfavourable distribution coefficient at high aqueous phase concentrations of solute, no results were obtained beyond an aqueous phase concentration of 0.072 M. Hence, it is questionable whether the mass transfer coefficient is constant in this region as is shown in Fig. 13.2 (at a value of 0.0018 cm/sec); additional points would be necessary before such a conclusion could be made. For this reason the results for this system will not be discussed further.

Fig. 13.3 indicates that as the aqueous phase concentration of phenol was increased the mass transfer rate remained constant until a critical value was reached. Beyond this the transfer rate increased

rapidly with increasing aqueous phase concentration of phenol, and this increase was accompanied with the onset of turbulence at the interface. The diffusional value of the mass transfer coefficient was found to be 0.0014 cm/sec.

The dependence of the mass transfer coefficient on the molar driving force ($C_B - C_B^*$) for the system benzene-acetic acid-water, with the direction of transfer from the benzene to the aqueous phase, is shown in Fig. 13.4 Fig. 13.5 shows the dependence for the benzene-phenol-water system with the direction of transfer from the aqueous continuous phase to the benzene phase.

It can be seen that both the driving force and the benzene phase inlet concentration affect the value of the mass transfer coefficient. For each solute inlet concentration in the benzene phase it is independent of the molar driving force of low value and until a critical value is reached. Beyond this critical point the mass transfer coefficient increases with increasing values of the molar driving force. In the case of acetic acid, Fig. 13.4, this increase is extremely rapid, whilst for phenol, Fig. 13.5, the increase is not so rapid. At sub-critical driving forces the value of the mass transfer coefficient is constant at 0.004 cm/sec for all acetic acid inlet concentrations in the benzene phase; for phenol it is constant at 0.0014 cm/sec.

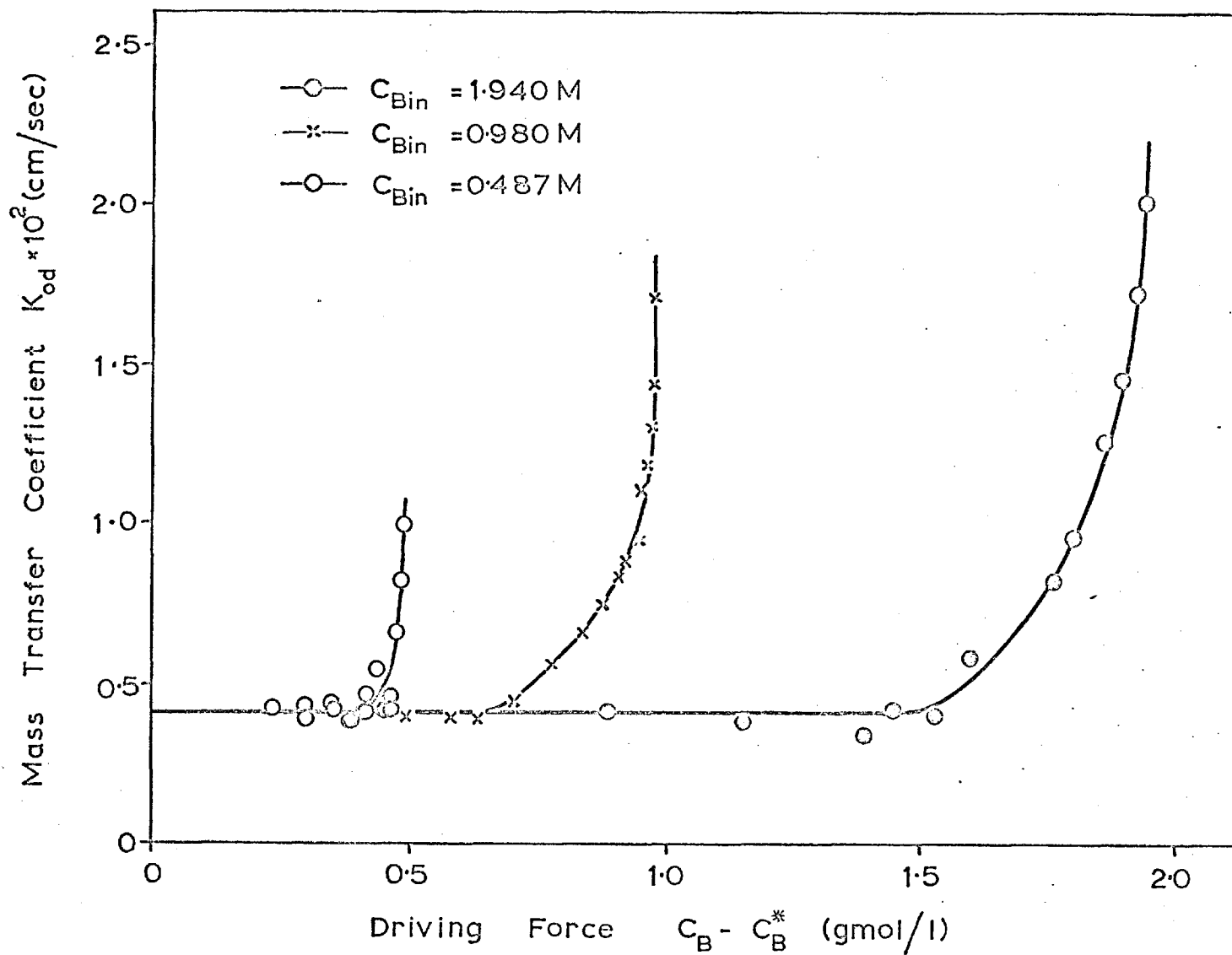


FIG. 13.4 : MASS TRANSFER COEFFICIENTS AS A FUNCTION OF DRIVING FORCE

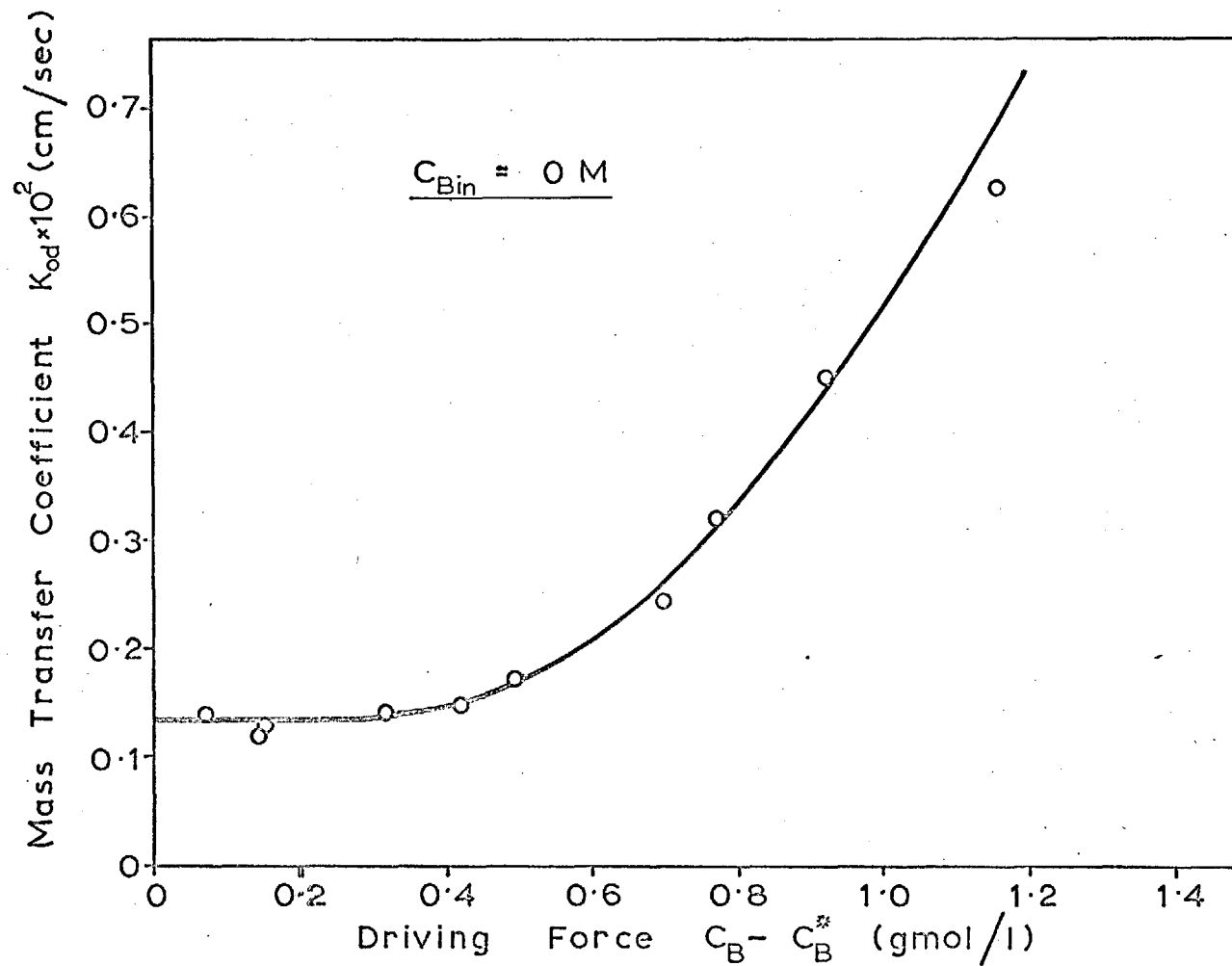


FIG.13.5 : MASS TRANSFER COEFFICIENTS AS A FUNCTION OF DRIVING FORCE

13.2 Correlation in Terms of Surface Pressure Changes.

Another way of expressing the results is to plot them as a function of the change in surface pressure, $\Delta\pi$. This is here defined as the difference between the equilibrium surface pressure corresponding to the composition at the interface π_i^* ($= \sigma_o - \sigma_i^*$) and the equilibrium surface pressure corresponding to the composition in the bulk of the drop π_b^* ($= \sigma_o - \sigma_b^*$), i.e.

$$\Delta\pi = \sigma_i^* - \sigma_b^* \quad \dots \quad 13.1$$

This model for the change in surface pressure assumes that the surface excess of solute is formed instantaneously when a fresh interface is formed by the arrival there of material with bulk concentration. This produces a rapid reduction in the interfacial tension resulting in movement in the interface. Hence, the propagation of the instability is assumed to be much quicker than the mass transfer process and the approach of the interface to equilibrium.

Fig. 13.6 shows the dependence of the mass transfer rate on the change in surface pressure for the transfer of acetic acid from the benzene to aqueous phase - for the three different concentrations of acetic acid in benzene - and for the transfer of phenol from aqueous to benzene phase (Table I of Appendix H). For the former system it can be seen that the mass transfer rate is initially constant for all inlet concentrations in the benzene phase and is independent of the change in $\Delta\pi$ up to a critical value. Beyond this critical point the mass transfer rate increases with increasing $\Delta\pi$, the rate of

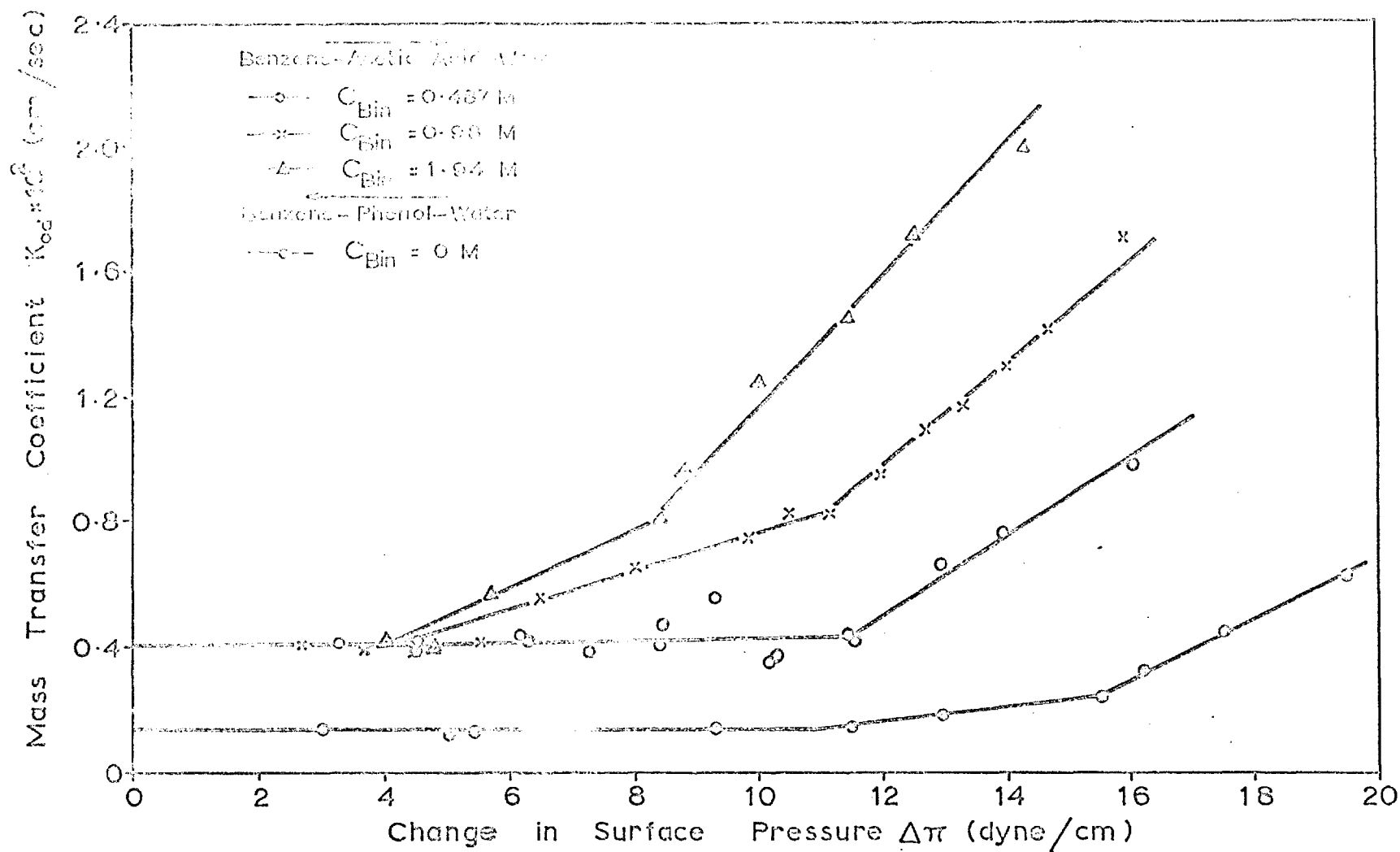


FIG. 13.6: MASS TRANSFER COEFFICIENTS AS A FUNCTION OF CHANGE IN SURFACE PRESSURE

increase differing for each inlet concentration in the benzene phase and the curves diverging from the critical value of $\Delta\pi$. Thus, it follows that a certain value of the surface pressure must exist, in this case 4 dynes/cm, before the mass transfer rate will increase. The curve showing the dependence for the transfer of phenol from aqueous to continuous phase is similar in shape to those described above. Again, it can be seen that a certain value of the surface pressure must exist before the mass transfer rate will increase, in this instance, 11 dynes/cm.

It is obvious from Fig. 13.6 that the above correlation is unsatisfactory and does not correlate the mass transfer coefficients for the regimes in which the curves are rising steeply. That is to say, the mass transfer coefficients in these regimes cannot be brought together to form a single curve as a function of the change in surface pressure (this was also the case using the molar driving force as the independent variable). However, this is not really surprising since this change in surface pressure represents only the driving force for the propagation of instability, whereas the resistance to movement in the interface has not been included. A complete description of the liquid behaviour at the interface can be arrived at only through the solution of the Navier-Stokes equation in which mass transfer has been accounted for. But this is hardly possible since the behaviour at the interface is extremely complex. Therefore, another approach had to be selected and an attempt has been made to investigate the influence of certain interfacial properties on the mass transfer coefficient.

13.3 The Effect of Interfacial Properties.

In order to compare the relative effects of the interfacial properties on the mass transfer coefficients, they are plotted with it on the same graph against the concentration of solute in the aqueous phase at the interface. The interfacial properties used in these plots are

- (a) the "surface strain" to which the interface is subjected, given by the ratio of the change in surface pressure to the surface compressional modulus, i.e. $\Delta\pi/M_i$.
- (b) the reciprocal of the surface viscosity, termed the "surface mobility", $1/\eta_{si}$.
- (c) the group $\Delta\pi/\eta_{si}$ which, by analogy with fluid flow through a pipe, is a measure of the velocity gradient introduced at the interface.

All value of η_{si} , M_i , and $\Delta\pi$ were determined under interfacial conditions, i.e. they correspond to the interfacial concentration of solute, and are given in Table I of Appendix A.

Figs. 13.7, 13.8 and 13.9 show the variation of mass transfer coefficient K_{od} , of surface strain $\Delta\pi/M_i$, of surface mobility $1/\eta_{si}$, and of the group $\Delta\pi/\eta_{si}$, with the concentration of acetic acid in the benzene phase at the interface, for the three different benzene inlet phase concentrations and with the direction of transfer from the benzene to the aqueous phase. From these curves it can be seen that the initial sharp decrease in K_{od} with increasing C_{wi} is accompanied by a similar decrease in $\Delta\pi/M_i$ and to a lesser extent by

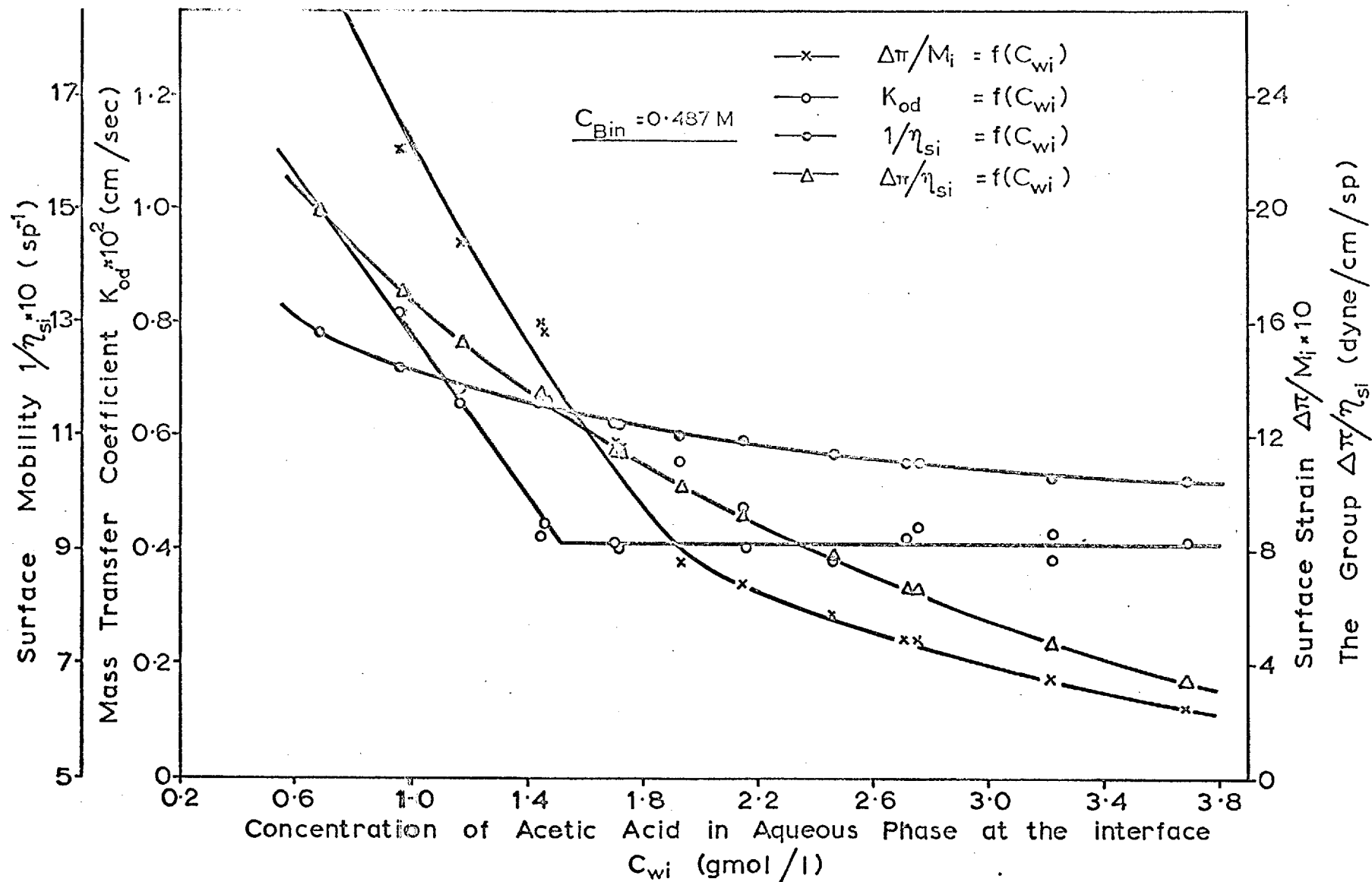


FIG. 13.7: MASS TRANSFER COEFFICIENT, SURFACE STRAIN, SURFACE MOBILITY, AND THE GROUP $\Delta\pi/\eta_{si}$ AS A FUNCTION OF INTERFACIAL CONCENTRATION

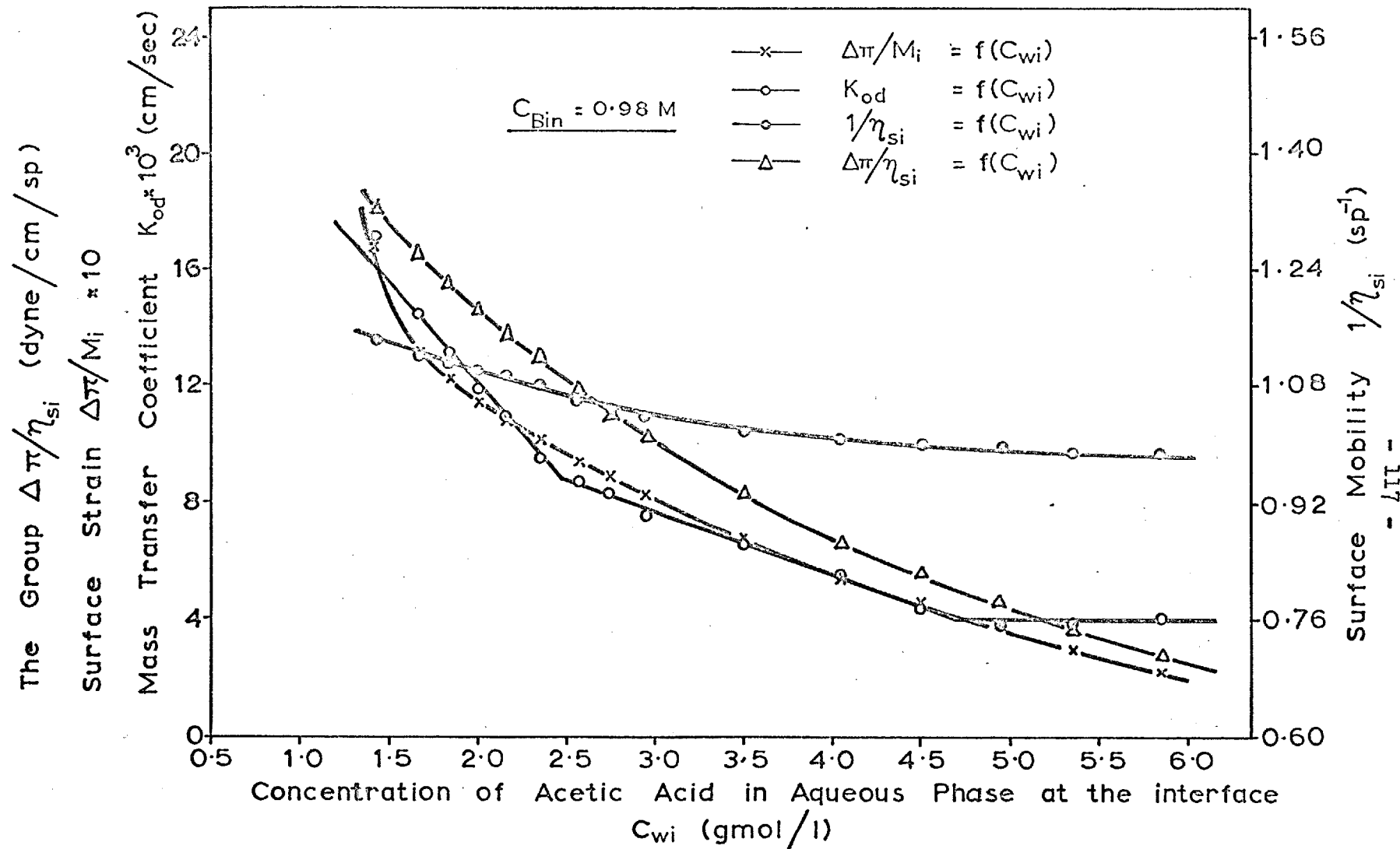


FIG.13.8: MASS TRANSFER COEFFICIENT, SURFACE STRAIN, SURFACE MOBILITY, AND THE GROUP $\Delta\pi/\eta_{si}$ AS A FUNCTION OF INTERFACIAL CONCENTRATION

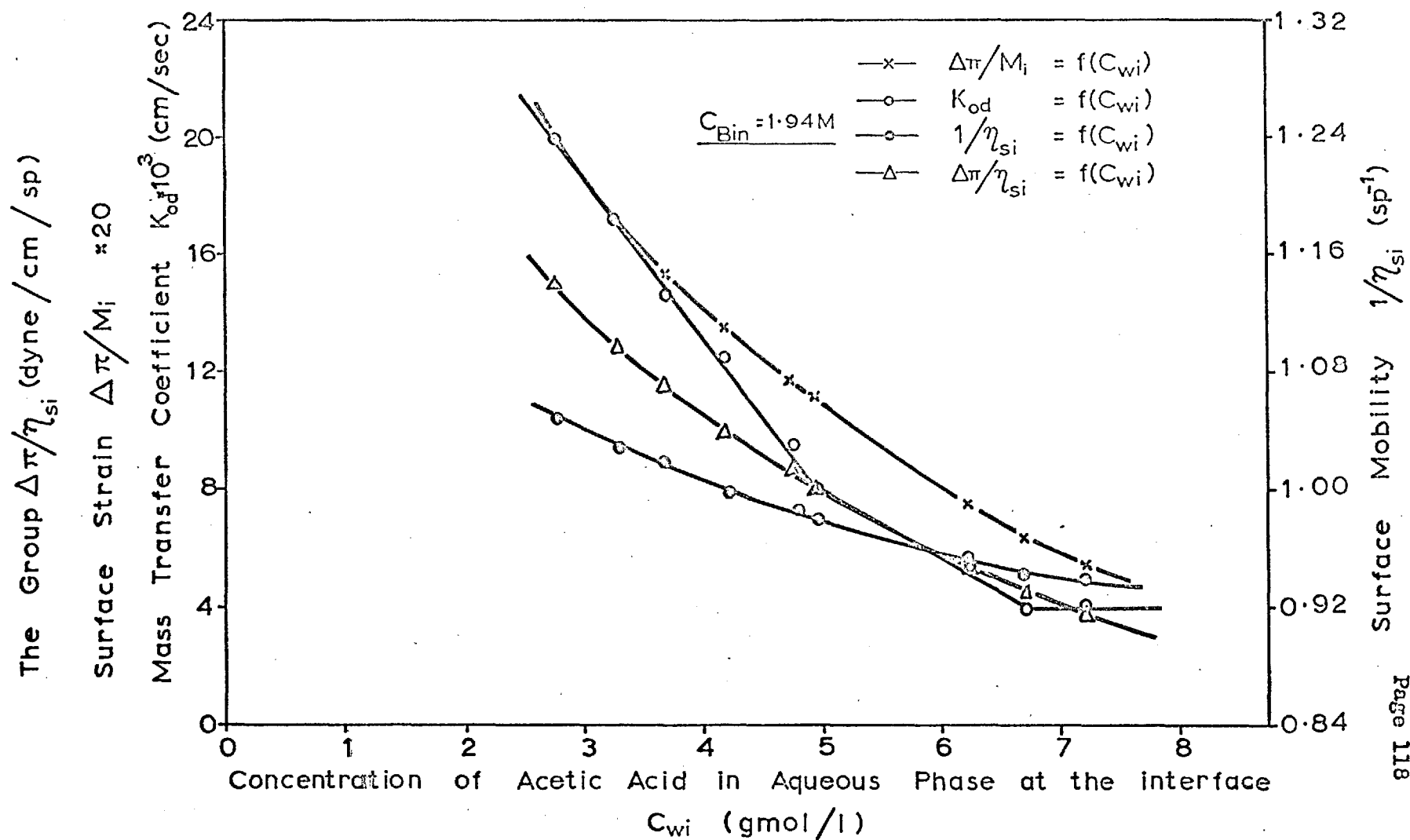


FIG. 13.9: MASS TRANSFER COEFFICIENT, SURFACE STRAIN, SURFACE MOBILITY, AND THE GROUP $\Delta\pi/\eta_{si}$ AS A FUNCTION OF INTERFACIAL CONCENTRATION

a decrease in $\Delta\pi/\eta_{si}$. On the other hand, the variation of $1/\eta_{si}$ over this range of C_{wi} is quite small, $1/\eta_{si}$ increasing slowly with increasing concentration of solute in the aqueous phase at the interface. Hence it appears that the surface mobility, the group $\Delta\pi/\eta_{si}$ and the surface strain all affect the mass transfer coefficient, but the critically controlling factor is the extent to which the interface is strained, as given by $\Delta\pi/M_i$.

Fig. 13.10 shows the dependence of the transfer of phenol from aqueous to benzene phase. Again, it can be seen that the $K_{od} - C_{wi}$ and $\Delta\pi/M_i - C_{wi}$ are similar in shape and concave upwards. Both K_{od} and $\Delta\pi/M_i$ are initially constant and independent of C_{wi} until a critical value of it is reached, beyond which both the mass transfer coefficient and the surface strain increase more or less at the same rate. On the other hand, $1/\eta_{si}$ decreases rapidly over the concentration range in which the mass transfer coefficient and the surface strain are constant, but thereafter remains constant whilst K_{od} and $\Delta\pi/M_i$ increase rapidly. In addition, the $\Delta\pi/\eta_{si} - C_{wi}$ curve is concave downwards, $\Delta\pi/\eta_{si}$ increasing in the concentration range in which the mass transfer coefficient and surface strain are constant. Thus the surface mobility and the group $\Delta\pi/\eta_{si}$ can both be said to have little or no effect on the rate of mass transfer, the critical factor being the strain to which the interface is subjected.

In an attempt to correlate the mass transfer coefficients in the regimes in which the curves are rising steeply, the coefficients

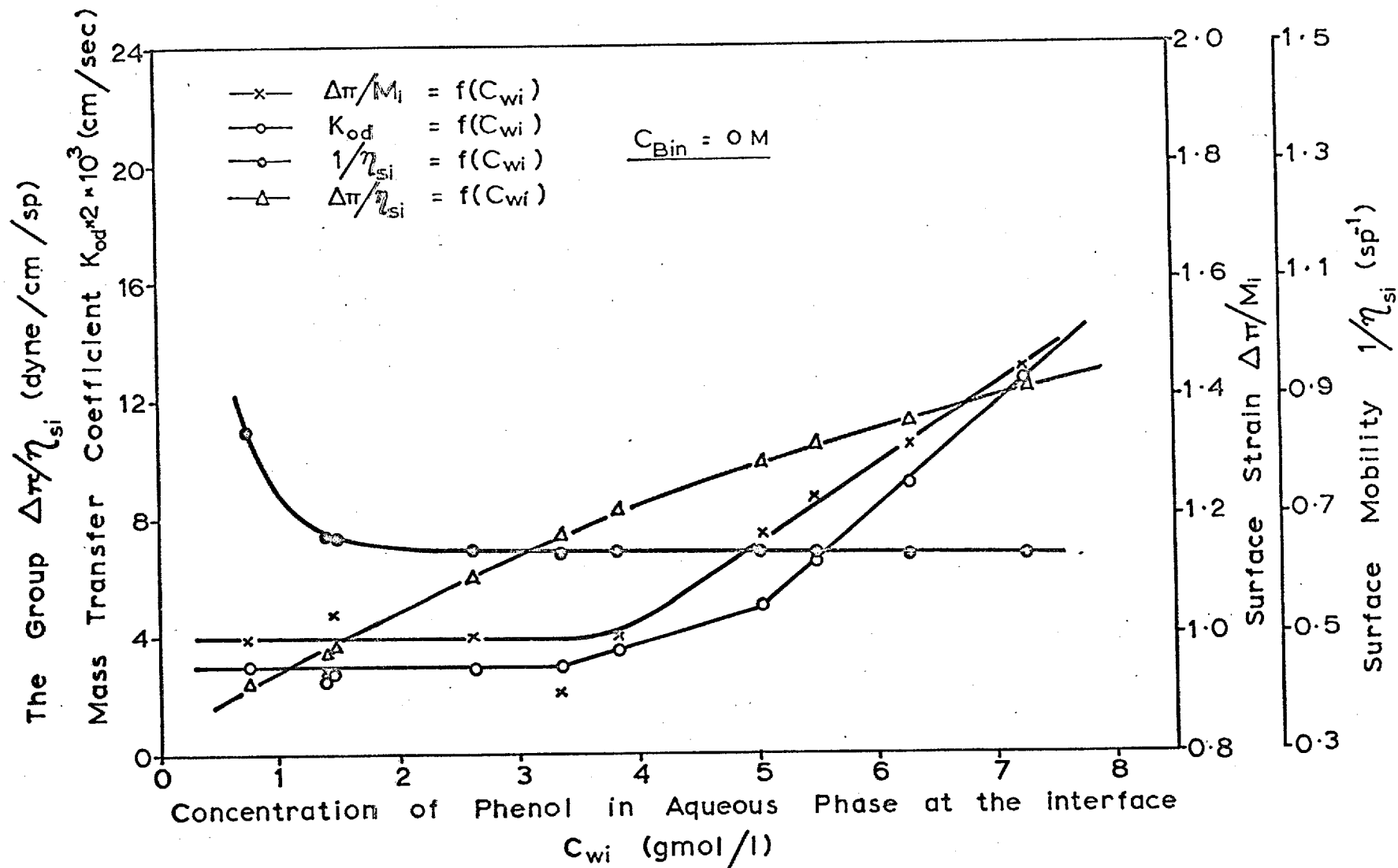


FIG.13.10: MASS TRANSFER COEFFICIENT, SURFACE STRAIN, SURFACE MOBILITY, AND THE GROUP $\Delta\pi/\eta_{si}$ AS A FUNCTION OF INTERFACIAL CONCENTRATION

were plotted against the surface strain. Fig. 13.11 shows the plots for the transfer of acetic acid from benzene to aqueous phase and for the transfer of phenol from aqueous to benzene phase. The curves are similar in shape to those of Fig. 13.6 and indicate that a certain value of the surface strain must exist before the mass transfer rate will increase. However, it is obvious, from Fig. 13.11, that the correlation is unsatisfactory for the regimes in which the curves are rising steeply.

13.4 New Model of Changes in Surface Pressure.

Since both the correlation in terms of interfacial properties and that in terms of surface pressure changes - based on the original model - proved unsatisfactory, the only possibility remaining was that this original model was in some way incorrect. Therefore, a new model has been developed for evaluating the changes in surface pressure when a fresh interface is formed by the arrival there of material of bulk concentration

In the previous model it was assumed that the surface excess of solute was formed instantaneously when a fresh interface was produced, and subsequently the propagation of the interfacial instability was much quicker than the mass transfer process and the approach of the interface to equilibrium. In the new model it is assumed that the surface excess of solute is not formed instantaneously but is built up over a period of time. This means that when surface renewal from within the bulk of the phase takes place at the interface, the

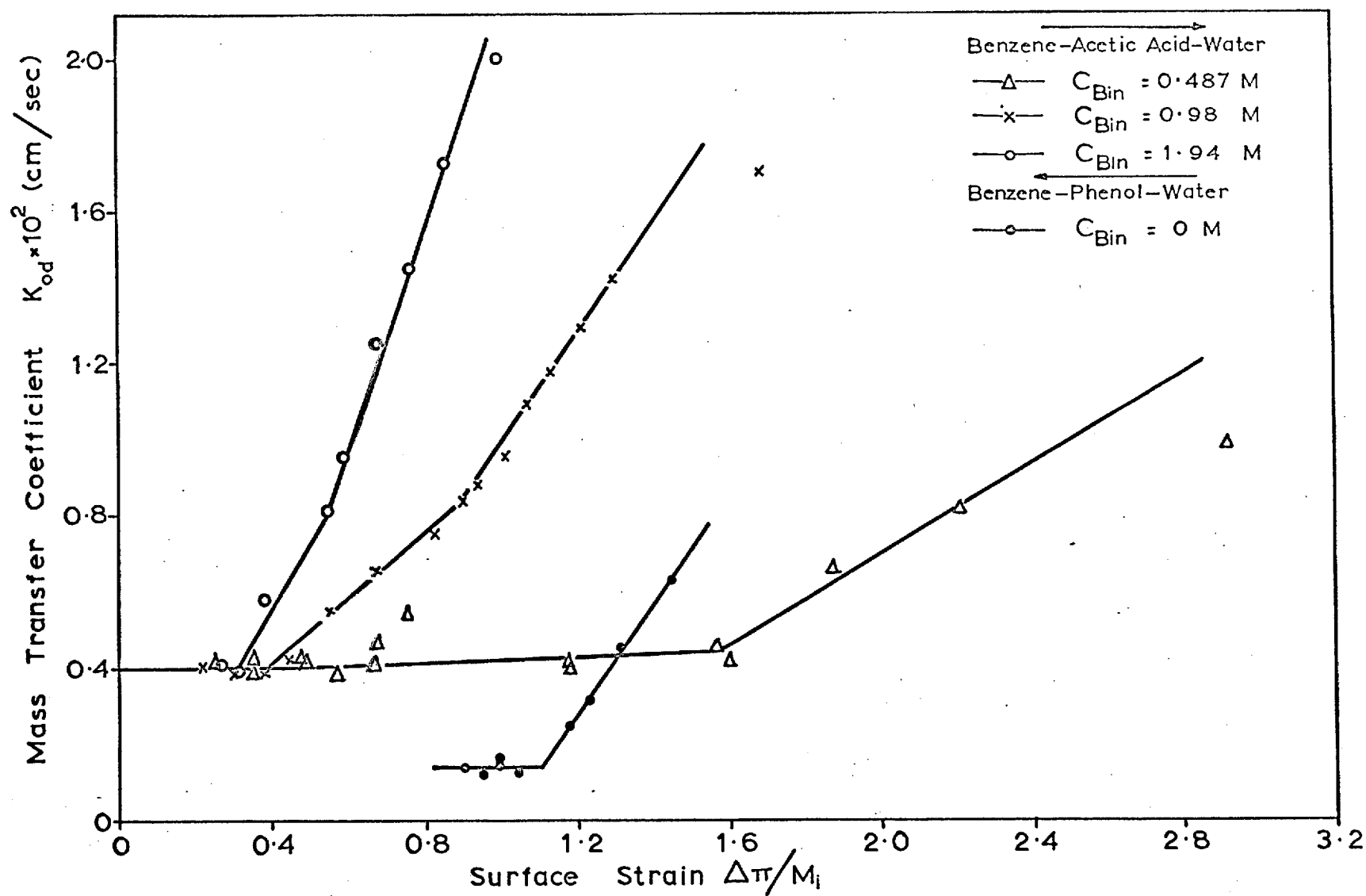


FIG. 13.11 · MASS TRANSFER COEFFICIENTS AS A FUNCTION OF THE SURFACE STRAIN

surface excess of solute already existing at the interface is destroyed and not instantaneously reformed. Hence, initially, there will be no local reduction of interfacial tension and consequently no movement in the interface. However, the surface excess now begins to build up accompanied with mass transfer between the two phases, since they are not in equilibrium. As this build-up occurs there will be a local reduction of interfacial tension which will produce movement in the interface. The change in surface pressure responsible for this movement will, therefore, be given by the difference between the equilibrium surface pressure corresponding to the composition of the solute at the undisturbed interface (i.e. before this initial mass transfer process) π_i^* ($= \sigma_o - \sigma_i^*$), and that corresponding to the composition at the interface after this initial mass transfer process, $\pi_i'^*$ ($= \sigma_o - \sigma_i'^*$), i.e.

$$\Delta\pi' = \pi_i'^* - \pi_i^* = \sigma_i^* - \sigma_i'^* \quad \dots \quad 13.2$$

where σ_i^* is the equilibrium interfacial tension corresponding to the composition at the undisturbed interface C_{wi} , and $\sigma_i'^*$ is that corresponding to the composition at the interface after the initial mass transfer process, C'_{wi} . It is assumed that the initial mass transfer process takes place between interfacial zones of composition C_{wb} and C_{Bi} or C_{Bb} and C_{wi} depending on the direction of mass transfer. This leads to the formation of new interfacial zones of composition C'_{wi} and C'_{Bi} which are in equilibrium.

For the transfer from benzene to aqueous phase the values of C'_{wi} were calculated from the equation

$$C'_{wi} = \frac{C_{wi} + C_B \sqrt{D_B/D_W} - b_i' \sqrt{D_G/D_W}}{1 + m_i' \sqrt{D_B/D_W}} \quad \dots \quad 13.3$$

using a trial and error method. This equation was obtained by replacing C_{wi} and C_w of equation 10.3 (page 81) by C'_{wi} and C_{wi} respectively. For the transfer from aqueous phase to benzene phase the corresponding equation is

$$C'_{wi} = \frac{C_w + C_{Bi} \sqrt{D_B/D_W} - b_i' \sqrt{D_B/D_W}}{1 + m_i' \sqrt{D_B/D_W}} \quad \dots \quad 13.4$$

The form of the results has been to plot a factor F against the change in surface pressure evaluated on the basis of the above model (Table I of Appendix I). This factor F is the ratio of the mass transfer coefficient to its value in the diffusional regime (which is constant). Fig. 13.12 shows this dependence for the benzene-acetic acid-water system, with the direction of transfer from the benzene to the aqueous phase and for three different benzene inlet phase concentrations. Allowing for a certain amount of scatter - particularly in what is termed the transitional regime - the values of F fall on the same curve. Initially F is constant and is independent of the change in surface pressure up to a critical value of it. Beyond this point F increases rapidly with increasing $\Delta\pi'$ and the increase is linear. Hence, it appears that a certain value of the surface pressure difference must exist before the mass transfer rate will increase; in this case the value is approximately 2.0 dynes/cm.

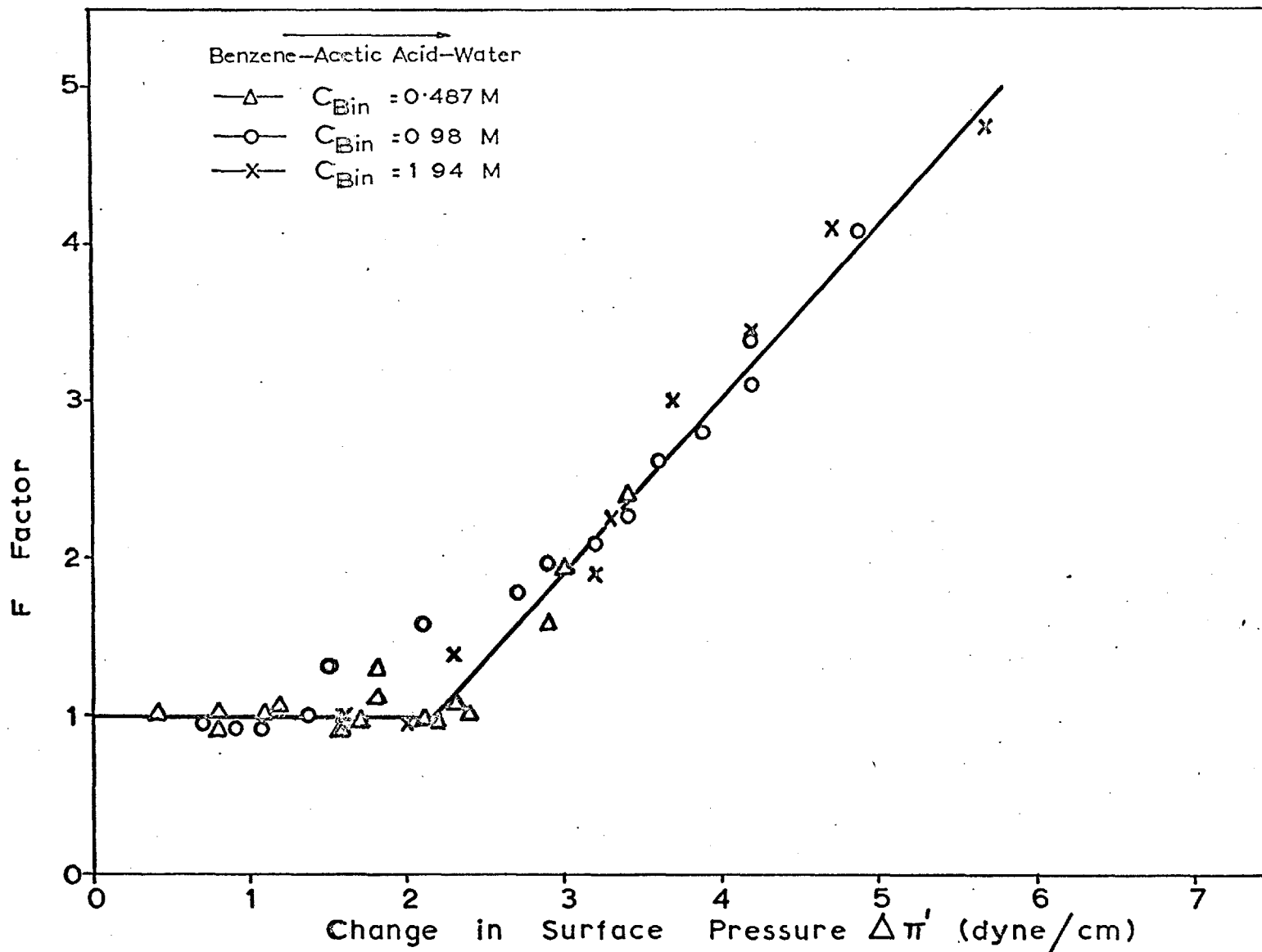


FIG. 13.12 : CORRELATION OF MASS TRANSFER COEFFICIENTS FOR ACETIC ACID ON BASIS OF NEW MODEL FOR CHANGES IN SURFACE PRESSURE

The results obtained for the transfer of phenol from the aqueous to the benzene phase also fall fairly close to this line.

B. Presence of Surface Active Agents.

With acetic acid transferring from the benzene to the aqueous phase (C_B in constant at 0.98 M and C_w constant at 0 M) investigations were carried out for the following five surface active agents, all soluble in the aqueous phase: dodecylamine hydrochloride, Teepol 514, Manoxol OT, sodium lauryl sulphate and Lissapol N.

13.5 Correlation in Terms of Changes in Surface Active Concentration.

The results (Table II of Appendix H) indicated that the mass transfer rate depended critically on the concentration of surface active agent in the aqueous phase. Since the dependence for each surface active agent is similar only that for Teepol 514 is shown here, the rest comprise Figs. H.1 - H.4 of Appendix H. Fig. 13.13 shows the variation of mass transfer coefficient with concentration in the aqueous phase of Teepol 514 and with aqueous phase concentration of acetic acid. The mass transfer rate rapidly decreased with increasing concentration of surface active agent, until the latter reached a critical value. This critical concentration differed for each surface active agent but in all cases its value was very small, for example, $20 \cdot 10^{-6}$ gm moles/litre for Teepol 514, and $3 \cdot 10^{-6}$ gm moles/litre for dodecylamine hydrochloride. Further increases in the aqueous phase concentration of surface active agent had no effect upon the value of the mass transfer coefficient which remained constant at 0.004 cm/sec

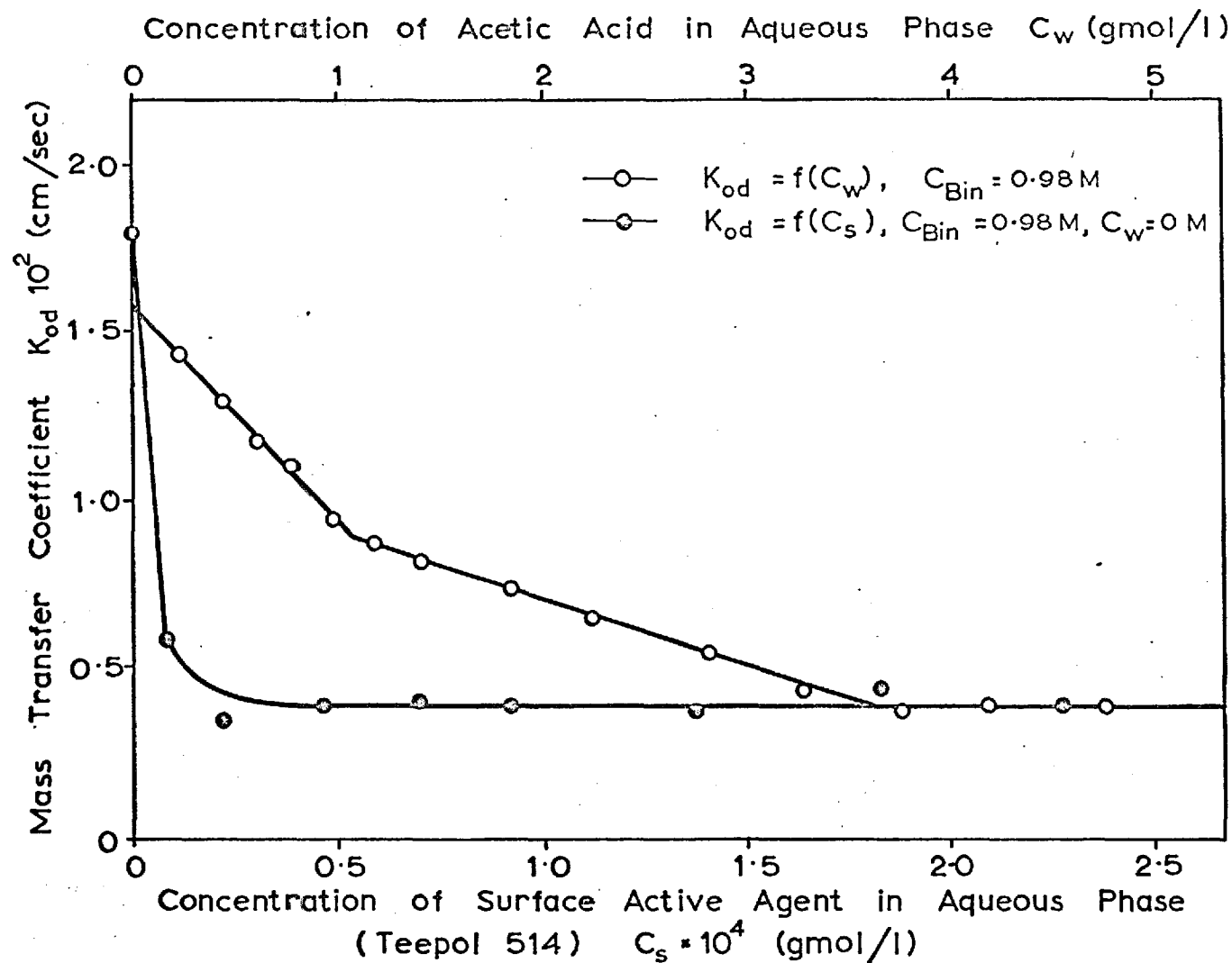


FIG. 13.13: EFFECT OF SURFACE ACTIVE AGENT ON THE MASS TRANSFER RATE

in all cases. Visual observations of the interface during each run confirmed the change from turbulent transfer - in the absence of surface active agent - to diffusional transfer with increasing surface active agent concentration.

13.6 Correlation in Terms of Surface Pressure.

The results may be expressed in another form by plotting the mass transfer coefficients as a function of the surface pressure, which is here defined as the lowering of interfacial tension caused by the surface active agent; that is to say $\pi = \sigma_0 - \sigma$, where σ_0 is the interfacial tension in the absence and σ that in the presence of surface active agent. For each of the five surface active agents the dependence of the mass transfer rate on the surface pressure is similar, thus only that for Teepol 514 is given here, Fig. 13.14, the rest appear in Appendix H, Figs. H.5 - H.8. The plots are similar to those for the mass transfer coefficient versus the concentration of surface active agent, and indicate that as the surface pressure increases so the mass transfer rate decreases rapidly, until a critical value of the surface pressure is reached. Further increases then have no effect on the mass transfer coefficient, which remains constant at 0.004 cm/sec, for all cases. The critical value of surface pressure differs slightly for each surface active agent, varying from 1.0 dyne/cm for dodecylamine hydrochloride to 2.5 dynes/cm for Manoxol OT.

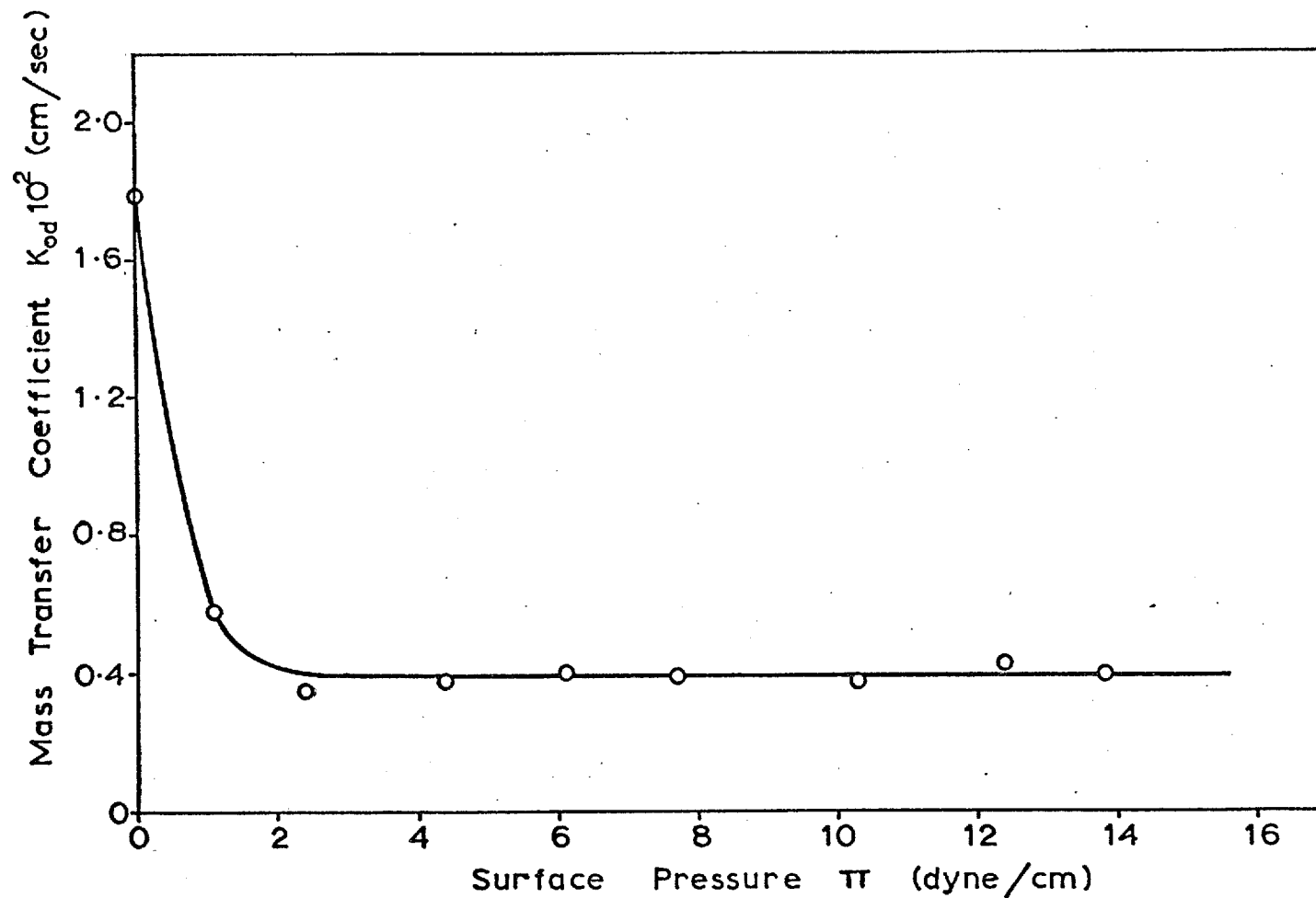


FIG.13.14: MASS TRANSFER COEFFICIENT AS A FUNCTION OF SURFACE PRESSURE
FOR SURFACE ACTIVE AGENT TEEPOL 514

13.7 Effect of Interfacial Properties.

To compare the relative effects of surface compressibility and surface mobility (the reciprocal of the surface viscosity) on the mass transfer rate, they were plotted, together with the mass transfer coefficient, against the concentration of surface active agent in the aqueous phase C_s (The experimental results are given in Table II of Appendix H).

The curves are all similar in shape and only that for sodium lauryl sulphate is given here, Fig. 13.15, the rest from Figs. H.9 - H.12 of Appendix H. The plots indicate that the rapid decrease in the mass transfer coefficient with increasing C_s is accompanied by a rapid decrease in the surface compressibility, for the curves are similar in shape, whilst over this same range of concentration the surface mobility decreases, but not nearly so rapidly. For example, Fig. 13.15 shows the bend in the surface mobility curve appearing at 2.5×10^{-6} gm mole/litre, and in the surface compressibility curve at 1.0×10^{-6} gm mole/litre; the corresponding bend in the mass transfer curve appears at 0.7×10^{-6} gm mole/litre. Hence, the graphs indicate that although both the surface mobility and the surface compressibility influence the mass transfer rate, the latter has the greater effect.

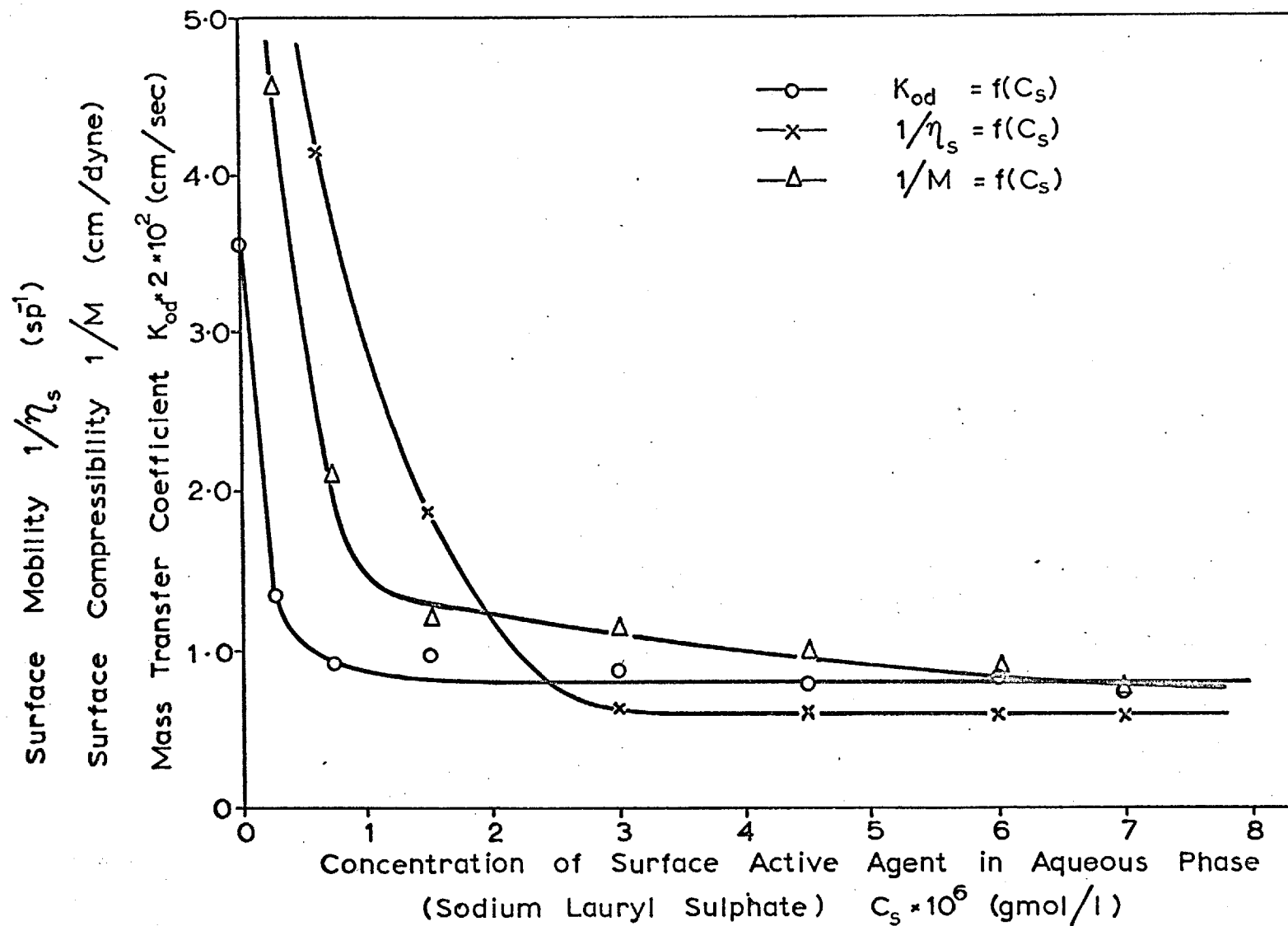


FIG. 13.15: MASS TRANSFER COEFFICIENT, SURFACE MOBILITY AND SURFACE COMPRESSIBILITY AS A FUNCTION OF SURFACE ACTIVE AGENT CONCENTRATION

14. DISCUSSION

In the previous chapter it has been shown that for a given solute concentration in the benzene inlet phase the mass transfer coefficient is independent of changes in surface pressure, up to a critical value of the surface pressure difference. In this region, termed the diffusional regime, the transfer is smooth and regular and takes place by molecular diffusion through the diffusional layer surrounding the droplet surface (cf Plate 3.1, page 17).

In the diffusional regime the results are in reasonably good agreement with the penetration theory. This was also found by Goltz² and he has dealt mathematically with the problem of mass transfer by pure diffusion, from growing drops, and arrived at an equation for the mass transfer coefficient, for actual, non-perfect drops,

$$K_{od} = 3.64\sqrt{D\pi/T_p} \quad \dots \quad 14.1$$

where K_{od} is the overall mass transfer coefficient, D is the coefficient of diffusion, $\pi = 3.142$, and T_p is the time for one pump revolution (the same pumps being used in this investigation).

For the system benzene-acetic acid-water the following values of the mass transfer coefficient were obtained:

Experimental 0.004 cm/sec.

From equation 14.1 ... 0.0048 cm/sec.

For the benzene-phenol-water system the values obtained were

Experimental	...	0.0014 cm/sec.
From equation 14.1	...	0.0045 cm/sec.

Although the agreement between the experimental and theoretical values of the mass transfer coefficient for the former system is very good, that for the latter is poor. A possible reason for the discrepancy in the benzene-phenol-water system is that, in addition to the likely error in the diffusion coefficient (only a single value for it could be found), the fractional extraction rate was exceedingly small (of the order of 2% or less). Hence the errors involved, particularly in the determination of concentration changes, could be very much larger than normal.

Although the curves in the diffusional regime are flat and in good agreement with the penetration theory it was difficult to find a theory for the regimes in which the curves are rising steeply. In these regimes the mass transfer coefficients were such that they could not be brought together to form a single curve as a function of any of the driving force, the change in surface pressure (based on the original model), or the interfacial properties. However, it has been possible to bring the mass transfer coefficients in these regimes. for the benzene-acetic acid-water system, to a single curve as a function of the change in surface pressure, based on a new model explained in the previous chapter.

The results for the pure solutes in the absence of surface

active agents indicate that the surface mobility and the group $\Delta\pi/\eta_{si}$ have little or no effect upon the rate of mass transfer. Insofar as the surface mobility is concerned, this is in agreement with the results of Davies & Mayers⁵⁰ using insoluble surface active agents, and was already predicted by Stuke⁶⁹. The controlling factor in the mass transfer process is the surface strain, given by the ratio of the change in surface pressure to the surface compressional modulus to which the interface is subjected, i.e. $\Delta\pi/M$. When the solute concentration is small $\Delta\pi/M$ is large and the interface is easily strained, that is to say surface renewal by eddies from within the bulk phase is relatively easy, and hence high mass transfer coefficients are observed. By contrast, when the solute concentration is high, $\Delta\pi/M$ is small and the interface is not easily strained, i.e. surface renewal is much more difficult, and mass transfer takes place by diffusion resulting in low values of the coefficient. The plots of K_{od} against $\Delta\pi/M$ (Fig. 13.11, p.122) indicate the transition from the "stagnant layer" diffusional process of Whitman to the general surface renewal mechanism of turbulent transfer.

Here it must be remembered that in the calculations of the modulus of compressibility the assumption was made that the rate of desorption of solute molecules at the interface is negligible compared with the rate of compression of the molecules. This may not be justifiable at high solute concentrations, and in the next chapter - dealing with recommendations for future work - it is suggested that this be looked into.

A most interesting feature of the effect of soluble surface active agents on the mass transfer coefficient is that - in all cases - the coefficient in the diffusional regime in the absence of surface active agents has the same value as that in the same regime in their presence. This provides evidence that the surface active agent has only a hydrodynamic effect, that is to say it influences the hydrodynamic conditions existing at the interface, and presents no direct barrier to mass transfer. This has been shown also by Boye-Christensen & Terjesen^{41,42} and Gordon & Sherwood⁵³.

The amount of surface active agent required to reduce the mass transfer coefficient to its diffusional value is, for all cases, extremely minute, e.g. $2 \cdot 10^{-6}$ gm mole/litre of dodecylamine hydrochloride. This amount of surface active agent is sufficient to reduce the coefficient by approximately 75%. This sharp decrease in the mass transfer coefficient is accompanied by a similar decrease in the surface compressibility, whilst over this same range of concentration the surface mobility decreases, but at a much slower rate. The indication is that the controlling factor in the mass transfer process is the surface compressibility. The surface active agent is preferentially absorbed at the interface between the two phases and tends to form a film around the droplet surface. Depending upon the concentration of surface active agent present the surface will have a certain "rigidity" or "elasticity". For very low values of surface active agent concentration the surface will be fairly elastic and

easily stretched; hence surface renewal by eddies from within the bulk of the droplet phase can take place and the mass transfer rate will remain high. However, as the surface active agent concentration increases the surface becomes more and more rigid and the eddies are damped (see Chapter 11, page 83) thus causing the rate of surface renewal to drop sharply. This will also be the case with the mass transfer coefficient. Eventually, at some critical concentration of surface active agent, the whole of the droplet surface will have become completely covered with surface active agent molecules tightly packed into the interface, and when this situation is reached surface renewal by eddies is no longer possible. When this occurs mass transfer can take place only by diffusion; then further additions of surface active agent have no effect on the mass transfer rate.

15. CONCLUSIONS

The main conclusions from the work can be summarised as follows:

1. The existence of three different regimes of mass transfer in liquid-liquid extraction - termed the diffusional, eruptive and turbulent regimes - has been confirmed; the type of transfer depending on the driving force and the magnitude of surface pressure gradients set up by local surface renewal.
2. The mass transfer coefficient in the diffusional regime is independent of the solute concentration and of changes in driving force and surface pressure. Its value can be predicted by the penetration theory.
3. Photographic observations of the interface during mass transfer in the eruptive regime, at speeds of up to 3,000 frames per second, have confirmed the movements in the interface explained in the text. An initial, tangential, outward movement is followed by a similar inward movement and, usually, by a normal ejection of solute into the bulk phase. This presents further proof for the eruptive mechanism.
4. For solutes in the absence of surface active agents, the surface mobility, the group $\Delta\pi/\eta_{si}$, and the surface strain to which the interface is subjected by eddies and movements in the bulk phase, all of these affect the mass transfer rate. Whereas the

effect of the first two factors is insignificant, the surface strain critically affects the transfer rate. Its value is given by the ratio of the change in surface pressure to the surface compressional modulus. A certain value of the surface strain must exist before the mass transfer rate will increase.

5. On the basis of a new model for evaluating the change in surface pressure at the interface, the mass transfer coefficients in the eruptive and turbulent regimes can be brought together to form a single curve as a function of the surface pressure difference, for the benzene-acetic acid-water system with the direction of transfer from the benzene to the aqueous phase. Further, a certain value of this surface pressure difference must exist, 2.0 dynes/cm in this case, before the mass transfer rate will increase.
6. Soluble surface active agents have a pronounced effect on the rate of mass transfer. If the solute concentration is such that operation is in the turbulent regime in the absence of surface active agent, the addition of only a minute amount will shift the mass transfer coefficient into the diffusional regime.
7. Beyond the critical value of the surface active agent concentration required to shift the transfer into the diffusional regime, further additions of surface active agent have no effect on the mass transfer rate.

8. The diffusional value of the mass transfer coefficient in the absence of surface active agent is the same as the diffusional value in its presence. This indicates that the surface active agent presents no direct barrier to mass transfer at the interface but that its effect is purely hydrodynamic in nature; i.e. it influences the hydrodynamic conditions existing at the interface by affecting values of surface viscosity, surface compressibility and surface pressure.
9. The addition of surface active agents has shown that surface compressibility is an important variable in inter-phase transfer, whereas surface viscosity - although affecting the transfer rate - is not a critical variable.

16. RECOMMENDATIONS FOR FUTURE WORK

16.1 Systems Studied

In the present investigation only two systems were studied, benzene-acetic acid-water and benzene-phenol-water. It is suggested that many more systems be studied, varying both the solute and the solvents used. At the same time the effect of such properties as solute diffusivity and viscosity could be determined.

16.2 Direction of Mass Transfer

The technique used in this work is easily adaptable for a study of mass transfer from the continuous to the dispersed phase. In this work the benzene-phenol-water system was the only one studied in this way.

16.3 Time of Drop Formation

It is suggested that the effect of time of drop formation be studied in each regime. The shorter the time of drop formation the greater the degree of turbulence within the drop; hence there will be a higher rate of surface renewal in turn affecting the value of the mass transfer coefficient.

16.4 Rate of Compression of Solute Molecules

In the calculation of the surface compressional modulus it was assumed that the rate of desorption of solute molecules at the interface was negligible compared with the rate of compression of the solute molecules. It is suggested that a quantitative photographic

analysis be made of the droplet surface, in an attempt to estimate this rate of compression of the solute molecules and hence to test the validity of the above assumption.

16.5 Equilibrium Data and Diffusion Coefficients

For accurate comparison of the results it is essential that reliable equilibrium data and diffusion coefficients are available. Empirical methods of predicting the latter may not be sufficiently accurate, since no account is taken of the variation with solute concentration.

16.6 Modification for Low Extraction

In order to improve the accuracy at low fractional extraction a differential method of analysis could be used, making use of a spectrophotometer, which has an accuracy of the order of 1%, for measuring and comparing the optical densities of the outlet and inlet phases. If an optical cell were incorporated in the outlet line from the second pump it would permit continuous analysis, and at the same time avoid evaporation during the transfer of samples.

17. LIST OF SYMBOLS AND UNITS.

A	...	surface coverage	... $\text{cm}^2/\text{molecule}$
$\bar{A}$	...	time mean area of one cycle	... cm^2
a	...	constant	
a'	...	activity of the solute	
α	...	constant	
b	...	constant	
β	...	constant	
C	...	concentration	... gm mole/litre
D	...	diffusivity	... cm^2/sec
d'	...	diameter of molecule	... cm
E	...	fractional extraction	
E_y	...	Young's Modulus	... dynes/cm^2
e	...	error	
F	...	flow rate	... cm^3/sec
g	...	acceleration due to gravity	... cm/sec^2
K	...	constant	
K_{od}	...	overall mass transfer coefficient	cm/sec
k	...	mass transfer coefficient for one phase	... cm/sec
k'	...	Boltzmann constant	
L	...	thickness of surface elements	... cm
M	...	surface compressional modulus	... dynes/cm
m	...	distribution coefficient	
N'	...	mass flux	... $\text{gm mole/cm}^2/\text{sec}$
$\bar{N}'$	...	mean mass flux	... $\text{gm mole/cm}^2/\text{sec}$
N	...	Avogadro number	... molecules/mole
n	...	constant	
p	...	constant	
Q	...	total quantity of solute transferred	... gm moles
R	...	Universal gas constant	ergs/deg/mole

Re	...	Reynold's number	
r	...	radius of nozzle tip	... cm
r'	...	constant	
Sc	...	Schmidt number	
Sh	...	Sherwood number	
s	...	fractional rate of surface renewal	
s'	...	constant	
T	...	Absolute temperature	... $^{\circ}\text{A}$
T_p	...	time for one complete pumping cycle	... secs
t	...	time	... secs
t_r	...	retardation	... secs
t'	...	constant	
u	...	constant	
V	...	drop volume	... cm^3
v	...	volume between nozzle tip and interface	... cm^3
z	...	distance	... cm
σ	...	interfacial tension	... dynes/cm
θ	...	time of drop formation or exposure	... secs
π	...	surface pressure	... dynes/cm
η_s	...	surface shear viscosity	... gm/sec (sp)
ρ	...	density	... gm/cm^3
Γ_s	...	surface excess of solute	... molecules/ cm^2
Γ_b	...	contribution of the bulk concentration	... molecules/ cm^2
$\phi(t)$	...	surface age distribution	

Suffixes

b ... in bulk of the phase
 B ... benzene phase
 c ... continuous phase
 d ... dispersed phase
 i ... at interface
 o ... in absence of solute or surface active agent
 s ... surface active agent
 w ... aqueous phase

Superscript

* ... at equilibrium

18. APPENDICES

APPENDIX A.

Key to Results Tables

F_w	... flow rate of aqueous phase	... cm^3/min
T_p	... time per pump revolution	... secs
$C_{B \text{ in}}$	... molar concentration of inlet benzene phase	... gm mole/litre
$C_{B \text{ out}}$	... molar concentration of outlet benzene phase	... gm mole/litre
C_{Bi}	... molar concentration of benzene phase at interface	... gm mole/litre
C_B^*	... equilibrium molar concentration of benzene phase	... gm mole/litre
C_w^*	... equilibrium molar concentration of aqueous phase	... gm mole/litre
C_{wi}	... molar concentration of aqueous phase at interface	... gm mole/litre
C_s	... molar concentration of surface active agent in aqueous phase	... gm mole/litre
K_{od}	... overall mass transfer coefficient	... cm/sec
t_r	... retardation time of talc particle	... secs
η_s	... surface viscosity	... gm/sec (sp)
η_{si}	... surface viscosity corresponding to concentration at interface	... gm/sec (sp)
$1/\eta_{si}$	... surface mobility	... sec/gm (sp^{-1})
A_i	... surface area available per molecule in the interface	... $\text{cm}^2/\text{molecule}$
M_i	... surface compressional modulus corresponding to the concentration at the interface	... dynes/cm
M	... surface compressional modulus	... dynes/cm
π	... surface pressure ($= \sigma_o - \sigma^*$)	... dynes/cm
σ^*	... equilibrium interfacial tension in the presence of surface active agent	... dynes/cm
σ_{Bb}^*	... equilibrium interfacial tension corresponding to the bulk concentration in benzene phase.	... dynes/cm

σ_{wb}^*	... equilibrium interfacial tension corresponding to bulk concentration in aqueous phase	... dynes/cm
σ_i^*	... equilibrium interfacial tension corresponding to concentration at the interface	... dynes/cm
$\Delta\pi$	... surface pressure difference = $\sigma_i^* - \sigma_{wb}^*$ or $\sigma_i^* - \sigma_{Bb}^*$ depending on direction of transfer	... dynes/cm
n	... slope of $\log \pi$ vs $\log C$ or π vs $\log C$ plots	
$\log \alpha$	... intercept of $\log \pi$ or π axis	
$\Delta\pi/M_i$	... surface strain	... sec/gm (sp. ⁻¹)

APPENDIX B

Table I - Absence of Surface Active Agents

Runs 1 - 43 ... Transfer of acetic acid from a benzene drop to water

Run	F_w	T_p	C_w	$C_{B \text{ in}}$	$C_{B \text{ out}}$	$K_{od} \cdot 10^2$
1	19.5	3.51	0.000	.496	.426	.994
2	19.9	3.50	.249	.496	.440	.816
3	20.3	3.51	.459	.496	.451	.658
4	20.2	3.49	.750	.496	.468	.421
5	20.0	3.48	.764	.487	.458	.446
6	18.8	3.52	1.019	.477	.451	.414
7	20.1	3.44	1.030	.496	.470	.409
8	19.9	3.51	1.264	.471	.438	.556
9	21.1	3.49	1.500	.496	.468	.475
10	20.4	3.51	1.509	.492	.468	.403
11	20.7	3.50	1.825	.496	.475	.380
12	19.2	3.51	2.103	.496	.474	.421
13	19.9	3.50	2.141	.484	.462	.441
14	20.6	3.49	2.645	.485	.467	.431
15	19.7	3.49	2.645	.484	.468	.386
16	20.9	3.52	3.145	.487	.473	.414
17	20.6	3.50	0.000	.980	.744	1.710
18	19.9	3.50	.226	.980	.783	1.43
19	19.9	3.52	.426	.980	.801	1.30
20	20.6	3.50	.604	.980	.819	1.18
21	19.9	3.50	.770	.980	.831	1.10
22	20.9	3.51	.975	.980	.853	.95
23	20.4	3.50	1.180	.980	.864	.88
24	20.1	3.51	1.398	.980	.872	.83
25	19.9	3.50	1.853	.980	.887	.75
26	19.2	3.50	2.240	.980	.902	.66
27	19.9	3.50	2.810	.980	.919	.56
28	20.1	3.49	3.293	.981	.942	.416
29	19.3	3.49	3.774	.980	.945	.387
30	19.6	3.50	4.195	.964	.933	.390
31	20.6	3.50	4.763	.984	.956	.402
32	20.8	3.50	0.000	1.940	1.393	2.00
33	19.8	3.49	.510	1.940	1.474	1.72
34	20.1	3.50	1.112	1.940	1.551	1.45
35	20.8	3.51	1.603	1.940	1.611	1.25
36	20.6	3.50	2.205	1.940	1.698	.951
37	20.4	3.51	2.617	1.940	1.740	.802
38	20.8	3.50	3.720	1.940	1.806	.584
39	19.5	3.51	4.234	1.960	1.872	.399
40	19.6	3.51	4.753	1.940	1.854	.419
41	19.5	3.50	5.253	1.970	1.902	.346
42	20.5	3.50	6.331	1.940	1.875	.398
43	20.0	3.49	7.438	1.950	1.897	.421

Runs 131 - 142 ... Transfer of phenol from a benzene drop to water

Run	F_w	T_p	C_w	$C_{B \text{ in}}$	$C_{B \text{ out}}$	$K_{od} \cdot 10^2$
131	20.1	3.50	0.000	1.115	1.035	.507
132	19.9	3.51	.050	1.114	1.039	.522
133	19.9	3.51	.100	1.117	1.071	.370
134	20.2	3.50	.200	1.074	1.065	.200
135	20.2	3.51	0.000	1.797	1.687	.432
136	20.2	3.51	.020	1.779	1.700	.323
137	19.9	3.50	.040	1.785	1.731	.226
138	20.0	3.50	.060	1.789	1.746	.185
139	19.7	3.50	.011	1.790	1.700	.362
140	20.1	3.51	.030	1.788	1.723	.258
141	19.9	3.51	.051	1.778	1.727	.215
142	20.1	3.51	.072	1.782	1.739	.186

Runs 144 - 153 ... Transfer of phenol from water to a benzene drop.

Run	F_w	T	C_w	$C_{B \text{ in}}$	$C_{B \text{ out}}$	$K_{od} \cdot 10^2$
144	20.5	3.50	.03	0.000	.0015	.142
145	20.0	3.50	.058	0.000	.0025	.120
146	20.0	3.50	.060	0.000	.0029	.133
147	20.2	3.51	.115	0.000	.0064	.143
148	20.2	3.50	.150	0.000	.0088	.149
149	20.0	3.50	.173	0.000	.0123	.176
150	20.1	3.50	.230	0.000	.0245	.248
151	20.1	3.50	.250	0.000	.0353	.325
152	20.2	3.50	.288	0.000	.059	.455
153	20.1	3.51	.345	0.000	.1032	.629

Table II - Presence of Surface Active Agents

Of the five surface active agents tabulated below, in each case the transfer was of acetic acid from a benzene drop to water.

Runs 44 - 51 ... Surface active agent - dodecylamine hydrochloride

Run	F_w	T_p	C_w	$C_s \cdot 10^6$	$C_B \text{ in}$	$C_B \text{ out}$	$K_{od} \cdot 10^2$
44	20.3	3.50	0	0.0	1.090	.817	1.775
45	19.9	3.51	0	.75	1.010	.873	.959
46	19.5	3.52	0	1.5	.990	.895	.679
47	19.6	3.49	0	2.25	.980	.927	.383
48	19.8	3.50	0	3.0	.980	.992	.419
49	20.0	3.49	0	4.5	.980	.922	.419
50	21.2	3.50	0	6.0	.980	.924	.405
51	21.0	3.49	0	7.5	.980	.923	.414

Runs 68 - 76 ... Surface active agent - Teepol 514

68	20.1	3.55	0	0.0	.980	.729	1.790
69	20.7	3.52	0	9.1	1.000	.917	.585
70	20.4	3.54	0	22.8	.990	.940	.354
71	19.0	3.54	0	45.6	.990	.935	.390
72	20.7	3.50	0	68.5	.992	.935	.406
73	20.6	3.50	0	91.3	.991	.935	.400
74	20.4	3.51	0	136.9	.987	.934	.380
75	20.2	3.51	0	182.5	.990	.929	.440
76	20.7	3.51	0	228.2	1.002	.944	.408

Runs 104 - 112 ... Surface active agent - Manoxol OT

104	20.1	3.50	0	0.0	.986	.727	1.830
105	19.9	3.51	0	0.3	.981	.842	1.001
106	20.0	3.51	0	0.75	.983	.876	.770
107	19.9	3.51	0	1.5	.996	.919	.546
108	20.1	3.52	0	2.25	.985	.924	.436
109	20.2	3.50	0	3.00	.992	.939	.385
110	20.0	3.50	0	4.50	1.012	.968	.309
111	20.0	3.51	0	6.0	1.012	.964	.335
112	20.0	3.48	0	7.5	1.012	.966	.324

Runs 113 - 121 ... Surface active agent - sodium lauryl sulphate

Run	F _w	T _p	C _w	C _s .10 ⁶	C _B in	C _B out	K _{od} .10 ²
113	19.9	3.50	0	0.0	.980	.734	1.780
114	20.5	3.50	0	0.3	.991	.899	.657
115	19.9	3.52	0	0.75	.980	.915	.467
116	20.1	3.51	0	1.50	.991	.922	.491
118	20.1	3.51	0	3.00	.991	.928	.449
119	20.0	3.51	0	4.50	.991	.935	.399
120	20.0	3.50	0	6.00	1.051	.956	.412
121	20.1	3.50	0	7.50	1.018	.965	.369

Runs 122 - 130 ... Surface active agent - Lissapol N

122	20.2	3.50	0	0.0	.980	.740	1.736
123	20.1	3.50	0	4.7	1.010	.928	.505
124	20.3	3.52	0	11.8	1.010	.950	.419
125	20.0	3.52	0	23.5	1.010	.953	.398
127	20.0	3.50	0	47.1	.988	.944	.315
128	20.0	3.50	0	70.6	.990	.937	.380
129	20.2	3.49	0	94.2	.987	.929	.420
130	20.3	3.50	0	117.9	.998	.944	.390

APPENDIX C

Table I - Equilibrium Data for the System Benzene-Acetic Acid-Water
at 25°C

Before Contacting			At Equilibrium		
C_B	C_W	Refractometer Reading	C_B^*	C_W^*	Volumetric Analysis gives C_W^*
.255	0	19 52 10	.005	.250	.249
.512	0	19 51 40	.011	.501	.500
.875	0	19 50 50	.025	.850	.850
1.115	0	19 50 00	.040	1.075	1.070
1.516	0	19 48 25	.066	1.450	1.45
1.740	0	19 46 27	.091	1.649	1.645
2.110	0	19 45 36	.110	2.000	2.005
2.389	0	19 43 58	.139	2.250	2.25
2.719	0	19 41 59	.170	2.549	2.54
3.010	0	19 39 30	.210	2.800	2.798
3.620	0	19 35 46	.270	3.350	3.35
4.750	0	19 24 45	.450	4.300	4.303
6.125	0	19 14 43	.615	5.510	5.505
7.365	0	18 59 40	.860	6.505	6.505
8.371	0	18 49 12	1.031	7.340	7.330
9.550	0	18 32 40	1.300	8.250	8.228

Table II - Equilibrium Data for system Benzene-Phenol-Water at 25°C

Before Contacting		At Equilibrium Sample of Sod.					
C_w	C_B	C_B^*	C_w^*	Organic Phase taken (mls)	Thios. soln. reqd. (mls)	Titration Difference (mls)	C_w^*
.0	0	0.0	.000	5	53.1	0.0	.000
.030	0	.020	.010	5	50.35	2.75	.009
.103	0	.073	.030	5	43.80	9.30	.031
.180	0	.130	.050	5	38.10	15.0	.050
.256	0	.185	.071	5	30.60	22.5	.075
.319	0	.234	.085	5	29.10	24.0	.080
.410	0	.300	.110	5	20.70	32.4	.108
.532	0	.392	.140	2	35.95	17.05	.143
.645	0	.480	.165	2	32.70	26.4	.170
1.005	0	.800	.205	1	40.50	12.6	.210
1.777	0	1.502	.275	1	36.10	17.0	.283
3.160	0	2.803	.357	1	32.30	20.90	.348
4.725	0	4.30	.425	1	28.50	24.6	.410
6.085	0	5.60	.485	1	25.00	28.1	.469
7.022	0	6.50	.522	1	22.70	30.44	.508

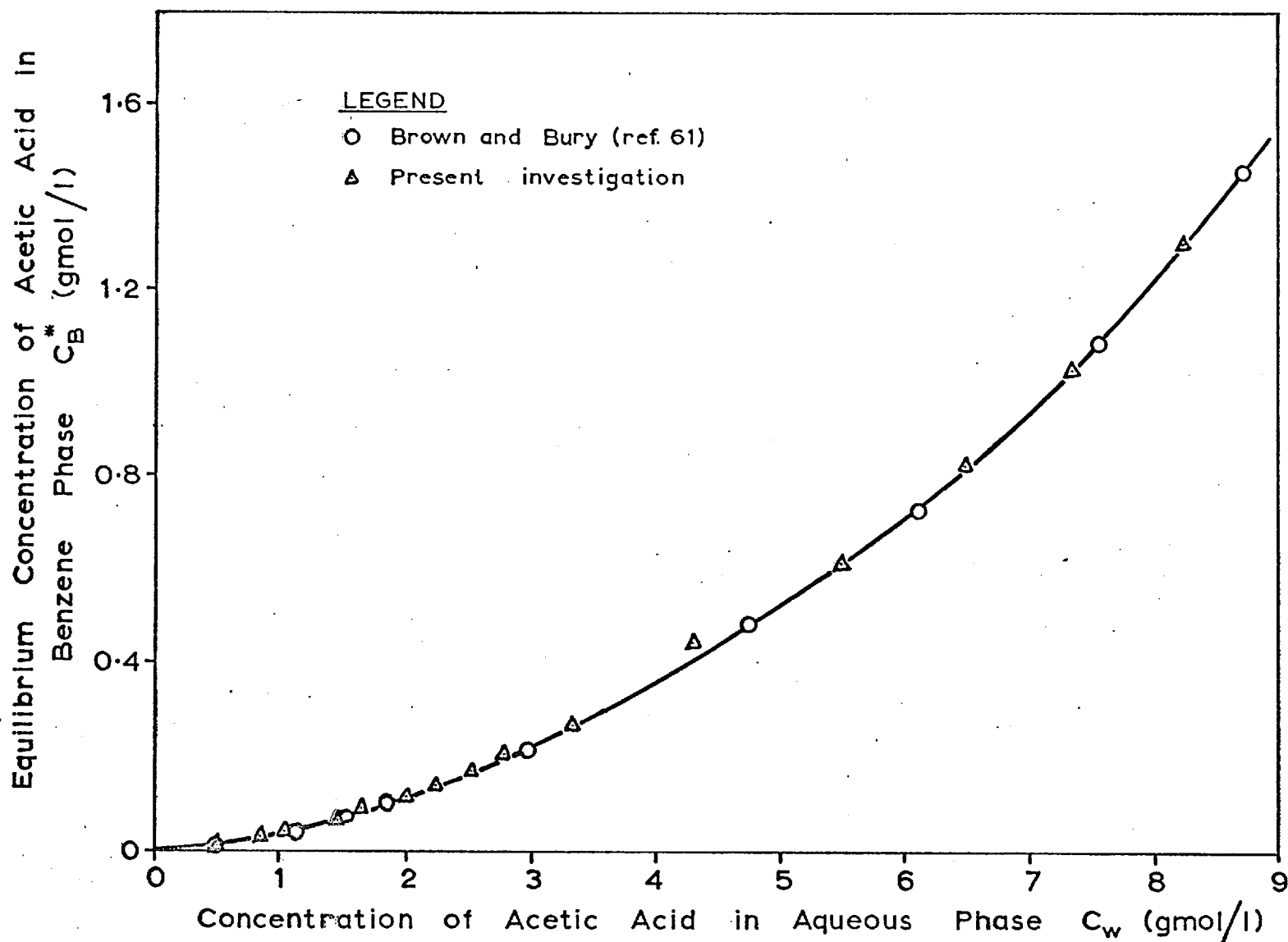


FIG.C.1: EQUILIBRIUM CURVE FOR BENZENE-ACETIC ACID-WATER SYSTEM AT 25°C

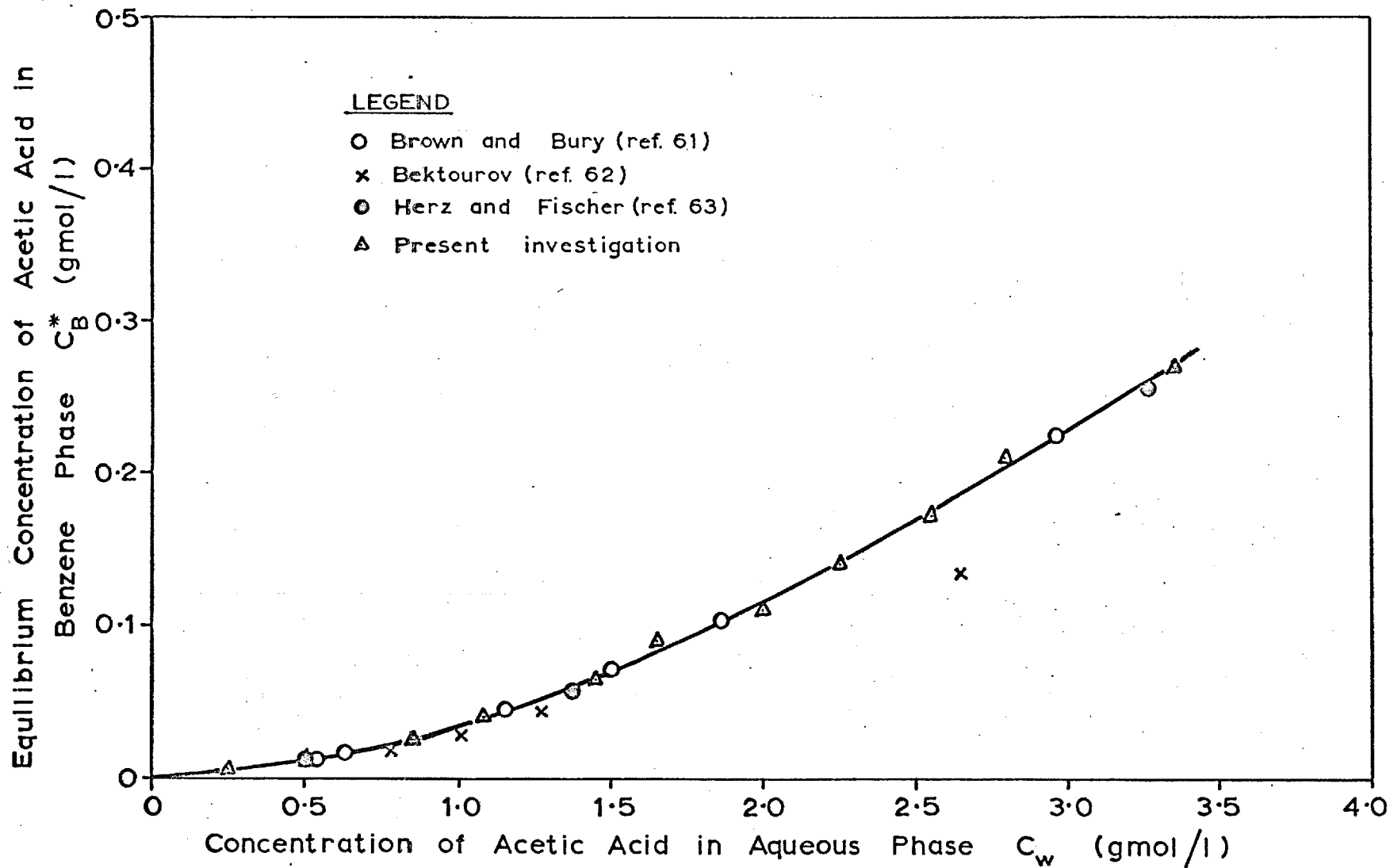


FIG.C.2:EQUILIBRIUM CURVE FOR BENZENE-ACETIC ACID-WATER SYSTEM AT 25°C

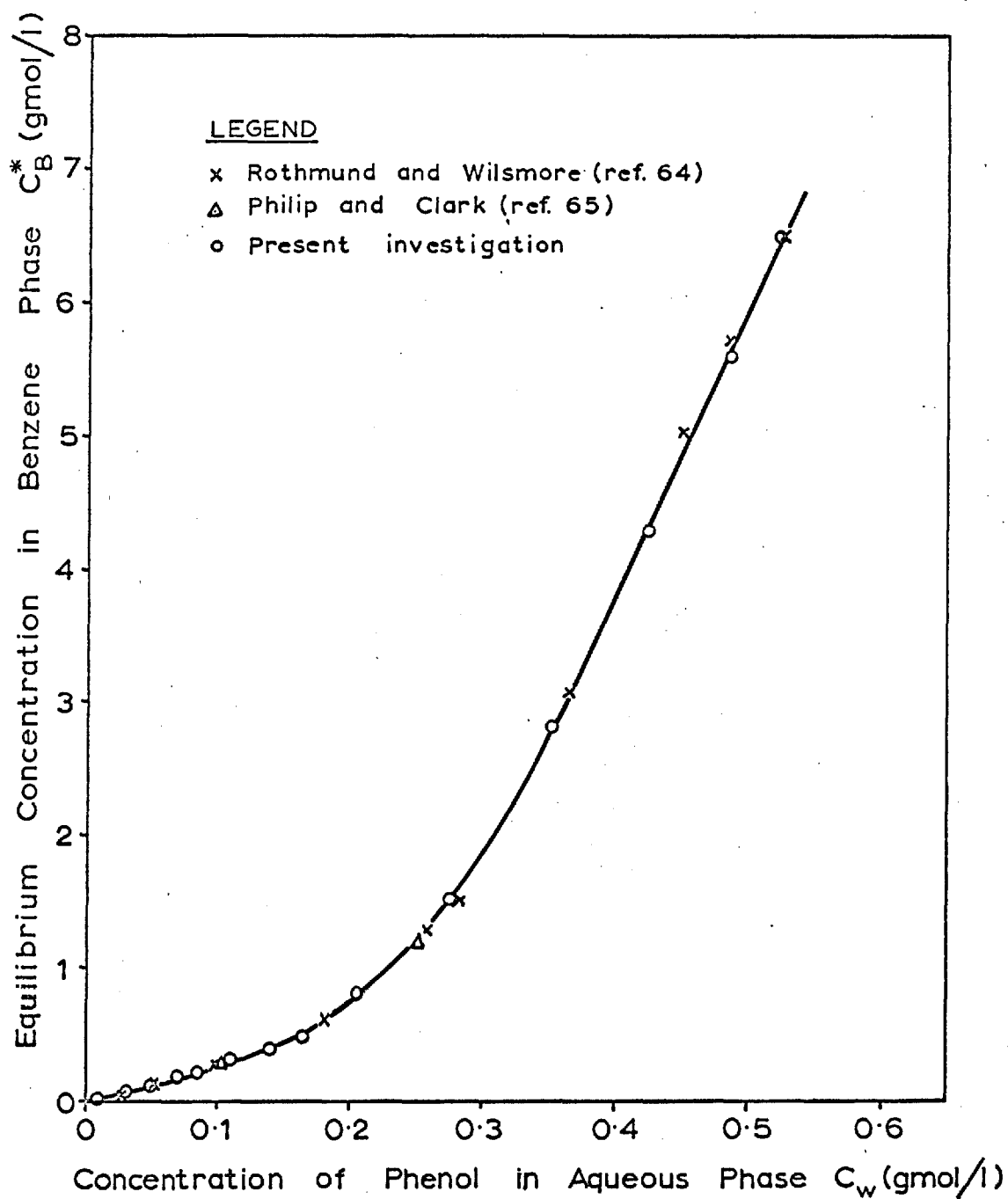


FIG.C.3:EQUILIBRIUM CURVE FOR BENZENE-
PHENOL-WATER SYSTEM AT 25°C

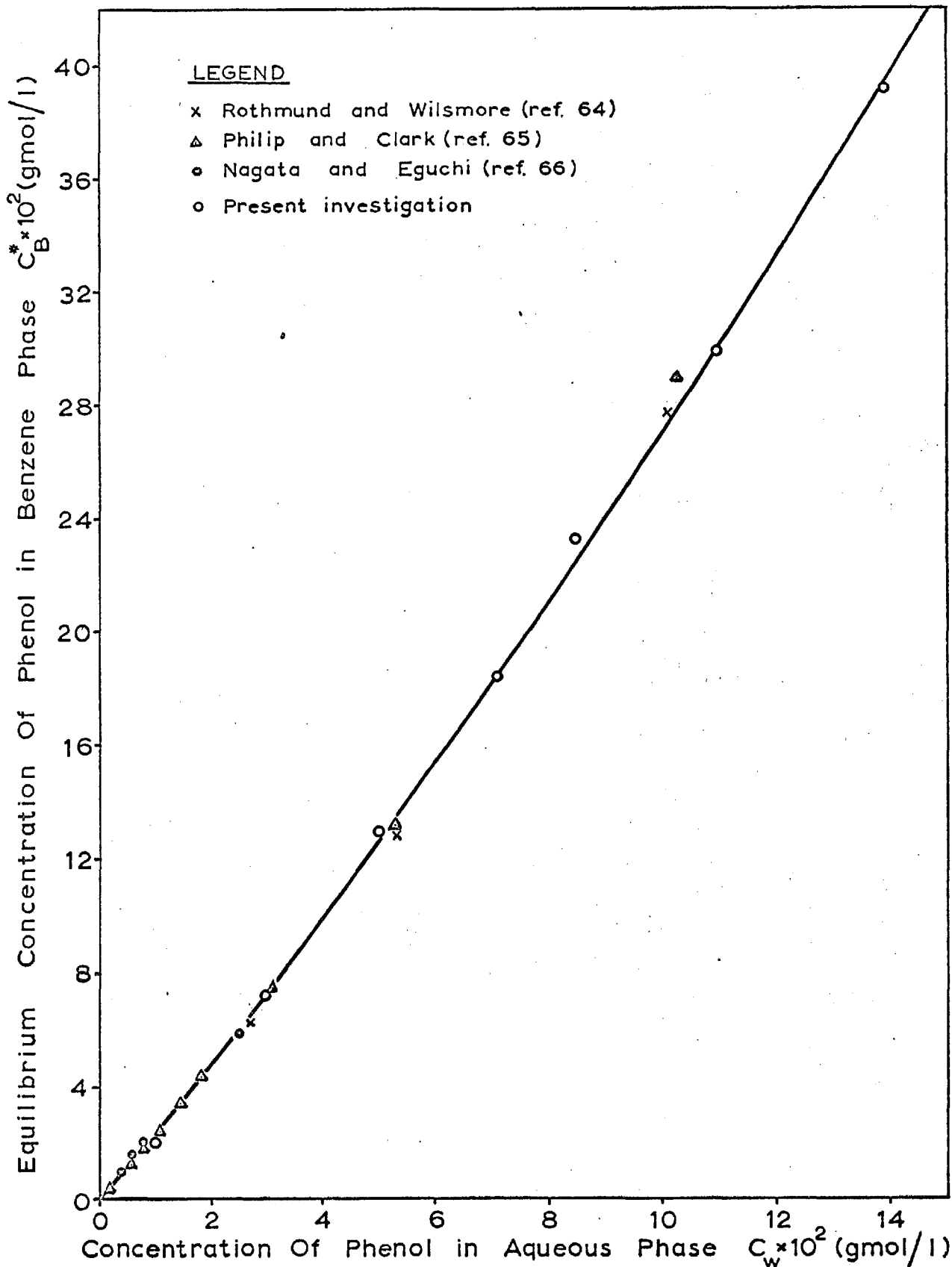


FIG.C.4: EQUILIBRIUM CURVE FOR BENZENE - PHENOL-WATER SYSTEM AT 25°C

APPENDIX D

Table I - Viscometer Calibration Results - Air-Water interface

Substance	$\eta_s \cdot 10^4$ (sp)	Time for 1 rev. (secs)			Mean (secs)	t_r (secs)
Clean water		98	99	98	98	
		100	96	95	97	
		98	100	102	100	
		100	97	101		
Stearic Acid at $23 \text{ }^{\circ}\text{A}^2$ on 0.01 N HCl	2.3	125	125	125	125	27
		126	125	124	125	27
		123	124	124	124	26
Stearic Acid at $20.1 \text{ }^{\circ}\text{A}^2$ on 0.01 N HCl	6.25	145	146	145	145	47
		150	152	151	151	53
		149	148	150	149	51
Stearic Acid at $20.1 \text{ }^{\circ}\text{A}^2$ on 0.001 N HCl	11.6	193	196	196	195	97
		190	193	196	193	95
		194	195	195	195	97
Octadecyl Alcohol at $20.8 \text{ }^{\circ}\text{A}^2$ on 0.01 N HCl	44.0	276	279	279	278	180
		265	269	273	269	171
		280	290	287	286	188
Octadecyl Alcohol at $20.8 \text{ }^{\circ}\text{A}^2$ on distilled water	380.0	565	570	569	568	470
		553	572	569	558	460
		568	570	566	568	470

Clean Benzene-Water interface

Revolution times of talc particle: 105 108 103 110 105 106
 .'. mean time = 106 seconds

Clean Ethyl Acetate-Water interface

Revolution times of talc particle: 100 102 98 99 105 103
 .'. mean time = 101 seconds

Table II - Surface Viscosity Results

A. Benzene-Acetic Acid-Water System

C_w^*	C_B^*	Mean Revolution Time of Talc Particle	t_r	$\eta_s \cdot 10^4$ sp
.238	.0053	112.0	6.0	.58
.764	.021	115.3	9.3	.87
1.49	.051	115.0	9.0	.85
1.656	.086	114.7	8.7	.80
1.999	.116	115.7	9.7	.90
2.406	.159	116.3	10.3	.98
2.810	.204	115.7	9.7	.90
3.650	.320	116.3	10.3	.98
4.300	.418	116.6	10.6	1.00
.500	.011	114.3	8.3	.74
.100	.003	109.3	3.3	.35
.000	.000	106	-	-

B. Benzene-Phenol-Water System

.010	.022	121	15	1.36
.020	.046	123	17	1.57
.030	.073	122	16	1.49
.040	.099	123	17	1.57
.050	.126	123	17	1.57
.090	.239	123	17	1.57
.110	.300	124	18	1.68
.005	.010	120	14	1.30
.002	.004	123	7	.68
.004	.008	117	11	1.0
.020	.046	123	17	1.57
.070	.182	123	17	1.57
.000	.000	106	-	-

C. Surface Active Agent - Dodecylamine Hydrochloride

$C_s \cdot 10^6$	Mean Revolution Time of Talc Particle	t_r	$\eta_s \cdot 10^4$ sp	$1/\eta_s$
.90	108	2	.20	5.0
1.80	109	3	.33	3.03
2.70	111	5	.50	2.0
3.60	118	12	1.10	.91
4.50	120	14	1.29	.775
5.40	121	15	1.33	.75
6.30	122	16	1.49	.67
7.20	121	15	1.33	.75
8.10	122	16	1.49	.67
0.00	106	-	-	-

D. Surface Active Agent - Teepol 514

13.7	110	4	.40	2.5
27.4	115	9	.80	1.25
54.8	129	23	2.04	.49
82.2	136	30	2.70	.37
109.6	137	31	2.80	.36
137.0	138	32	2.92	.34
164.4	140	34	3.17	.32
191.8	139	33	3.02	.33
0.0	106	-	-	-

E. Surface Active Agent - Manoxol OT

.42	111	5	.50	2.0
.84	112	7	.58	1.72
1.26	115	9	.80	1.25
1.68	118	12	1.15	.88
2.10	124	18	1.67	.60
2.52	123	17	1.61	.62
3.36	124	18	1.67	.60
4.26	125	19	1.73	.58
5.04	126	20	1.84	.54
5.88	127	21	1.95	.51
0.0	106	-	-	-

F. Surface Active Agent - Lissapol N

$C_s \cdot 10^6$	Mean Revolution Time of Talc Particle	t_r	$\eta_s \cdot 10^4$ sp	$1/\eta_s$
8.9	119.5	13.5	1.25	.8
17.9	126.0	20.0	1.76	.58
26.9	128.5	22.5	2.00	.50
35.8	129.5	23.5	2.09	.48
44.8	123.5	17.5	1.54	.65
53.7	128.5	22.5	2.00	.50
71.6	129.5	23.5	2.09	.48
89.5	129.0	23.0	2.04	.49
107.4	131.0	25.0	2.20	.45
4.5	115.0	9.0	0.80	1.25
0.0	106.0	-	-	-

G. Surface Active Agent - Sodium Lauryl Sulphate

0.6	111	5	.50	2.0
1.2	110	4	.40	2.5
1.8	113	7	.67	1.49
2.4	117	11	1.07	0.93
3.0	121	18	1.67	0.60
3.6	124	18	1.67	0.60
4.8	127	21	1.85	0.54
6.0	124	18	1.67	0.60
0.0	106	-	-	-

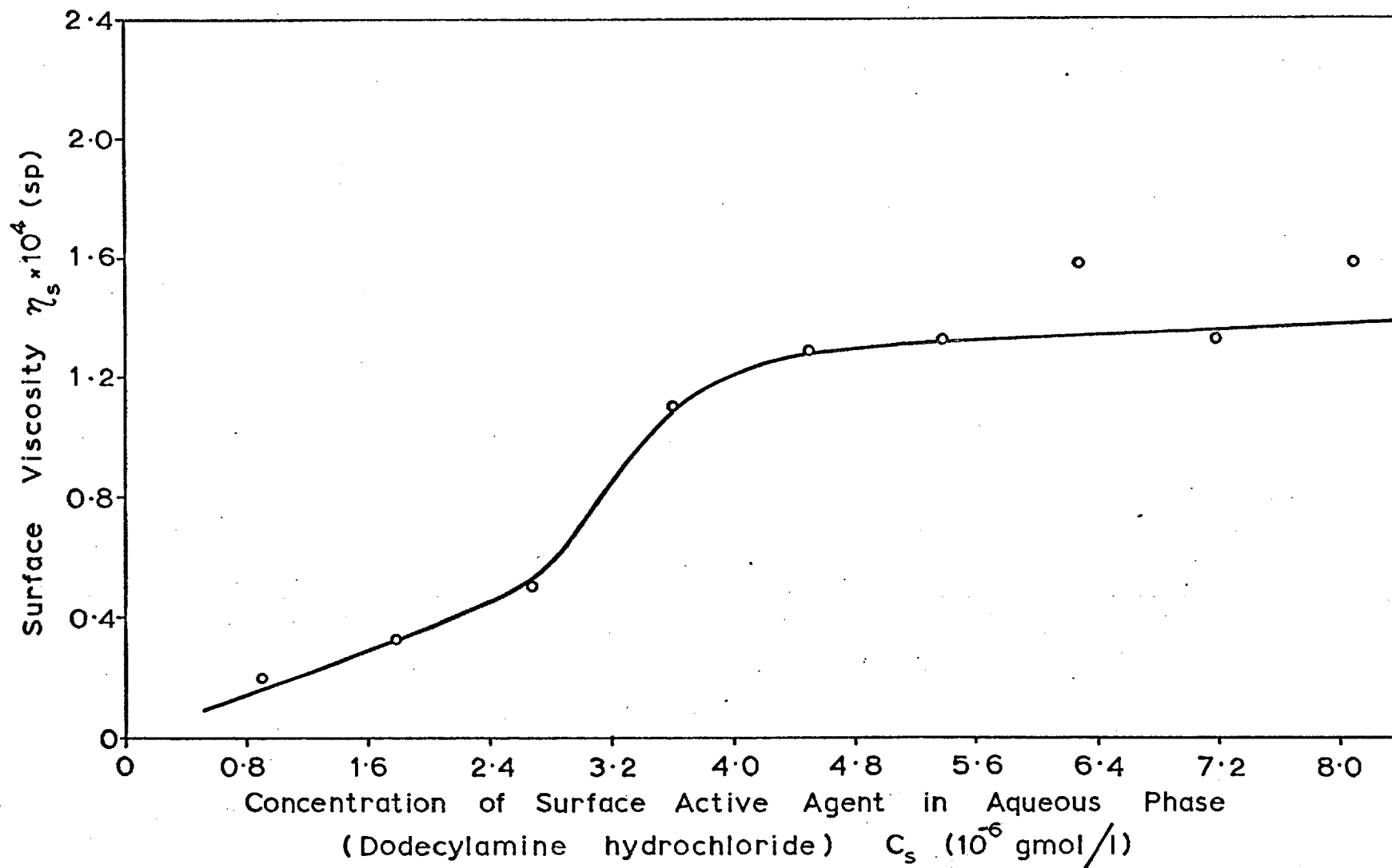


FIG.D.1: VARIATION OF SURFACE VISCOSITY WITH CONCENTRATION OF SURFACE ACTIVE AGENT DODECYLAMINE HYDROCHLORIDE

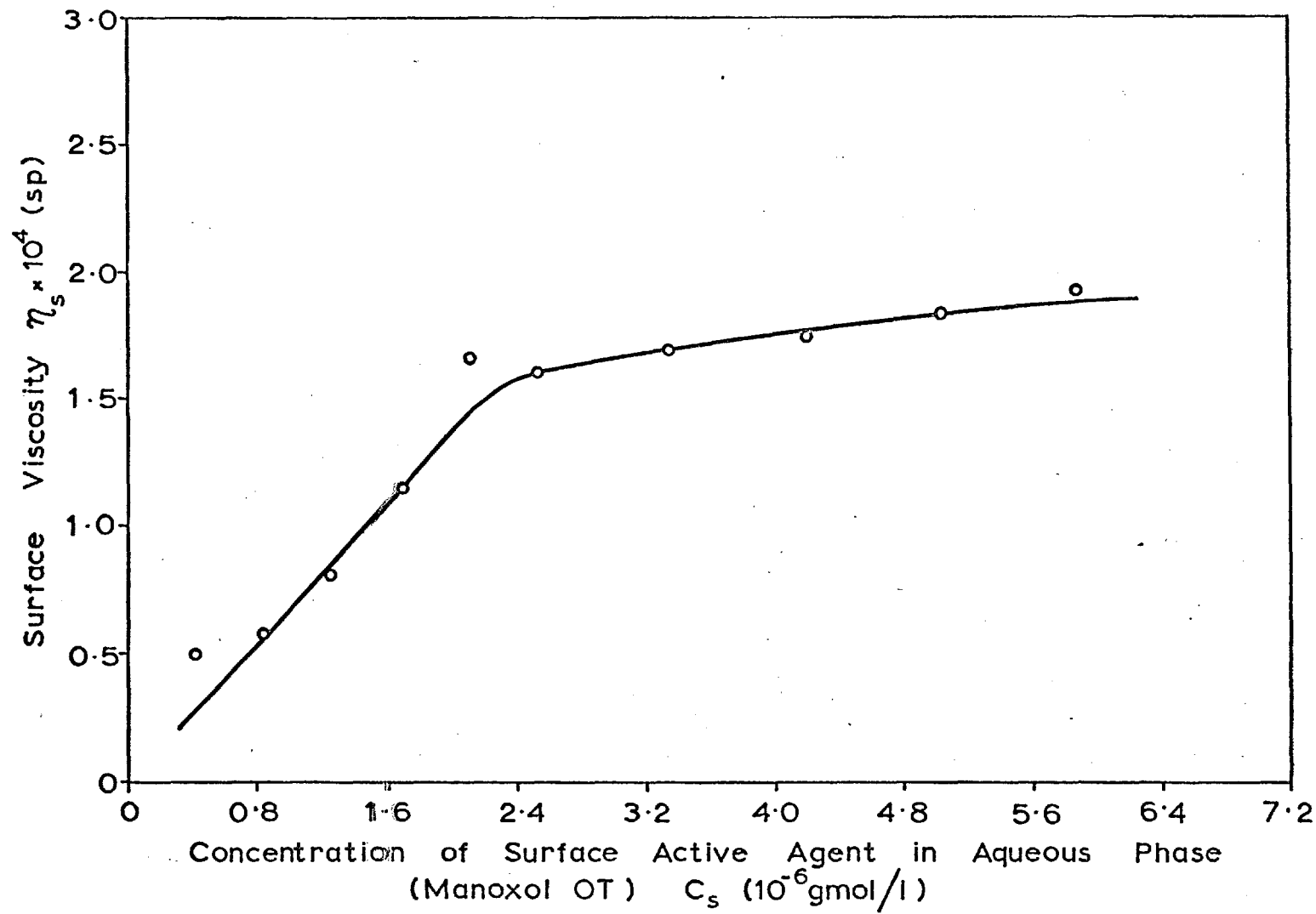


FIG.D.2: VARIATION OF SURFACE VISCOSITY WITH CONCENTRATION OF SURFACE ACTIVE AGENT MANOXOL OT

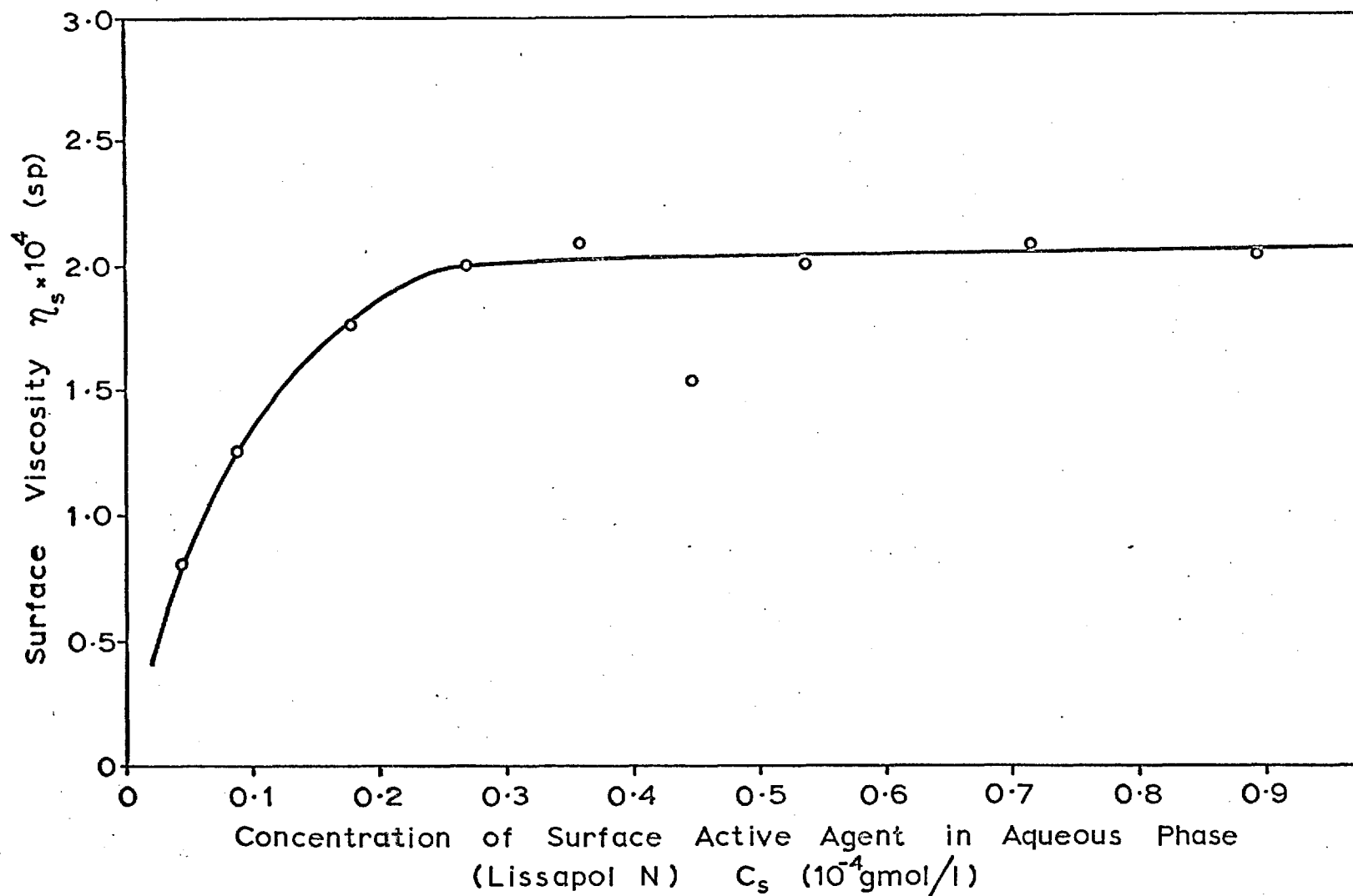


FIG.D.3: VARIATION OF SURFACE VISCOSITY WITH CONCENTRATION OF SURFACE ACTIVE AGENT LISSAPOL N

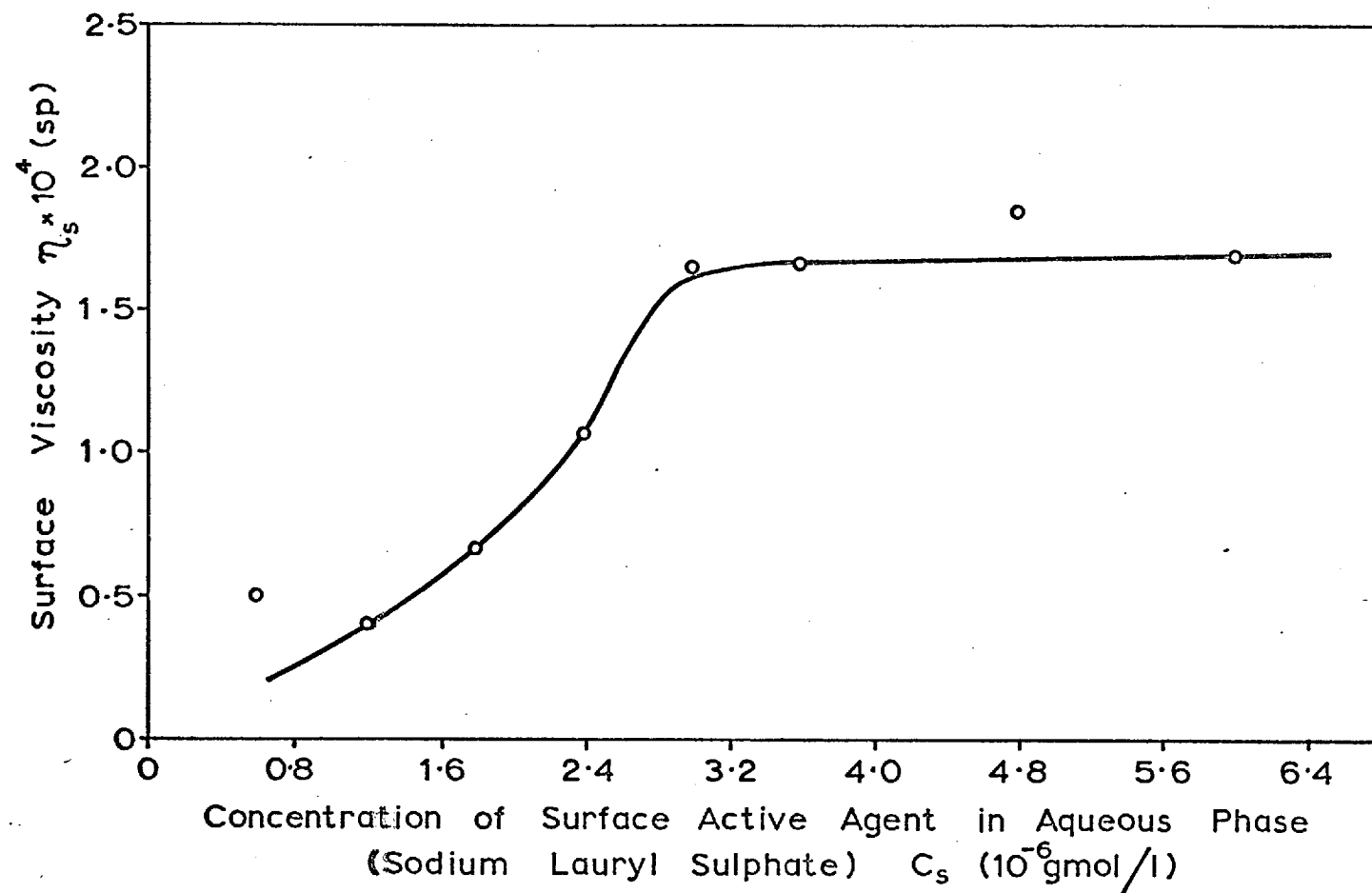


FIG.D.4 : VARIATION OF SURFACE VISCOSITY WITH CONCENTRATION OF SURFACE ACTIVE AGENT SODIUM LAURYL SULPHATE

APPENDIX E

Interfacial Tension Results

A. Benzene-Acetic Acid-Water System

C_B^*	C_W^*	σ^*
.000	.000	34.2
.005	.226	31.5
.0095	.426	29.7
.015	.604	28.4
.021	.770	27.4
.032	.925	26.1
.046	1.186	25.0
.059	1.348	24.0
.100	1.853	21.9
.143	2.240	20.4
.206	2.810	18.3
.270	3.293	16.5
.385	3.774	15.3
.400	4.195	14.2
.490	4.763	12.9
.575	5.253	11.8
.782	6.331	9.7
1.057	7.438	7.7

B. Benzene-Phenol-Water System

C_B^*	C_W^*	C^*
.000	.000	37.5
.020	.010	35.8
.073	.030	33.8
.130	.050	30.9
.185	.071	29.15
.234	.085	27.2
.300	.109	25.15
.392	.140	24.45
.480	.165	22.35
.700	.195	18.0
1.11	.240	13.1
2.00	.309	11.1
1.412	.266	13.5
1.732	.286	12.4

C. Surface Active Agent Dodecylamine Hydrochloride

$C_s \cdot 10^6$	σ^*
.00	35.2
.75	34.5
1.5	34.2
2.25	33.9
3.0	33.6
4.5	33.5
6.0	33.0
7.5	32.7

D. Surface Active Agent Sodium Lauryl Sulphate

$C_s \cdot 10^6$	σ^*
.00	35.2
.30	35.1
.75	34.75
1.5	34.4
3.0	33.75
4.5	33.2
6.0	32.85
7.5	32.5

D. Surface Active Agent
Teepol 514

$C_s \cdot 10^4$	σ^*
.000	35.1
.091	34.0
.228	32.7
.456	30.9
.685	28.9
.913	27.15
1.369	25.2
1.825	22.45
2.282	22.2

E. Surface Active Agent
Lissapol N

$C_s \cdot 10^5$	σ^*
.000	35.2
.471	34.2
1.179	33.25
2.355	31.5
4.71	29.75
7.065	28.55
9.42	28.0
11.79	27.7

F. Surface Active Agent
Manoxol OT

$C_s \cdot 10^6$	σ^*
0.0	35.2
0.3	34.0
0.75	34.2
1.5	34.1
2.25	33.9
3.0	31.8
4.5	31.2
6.0	30.9
7.5	29.8

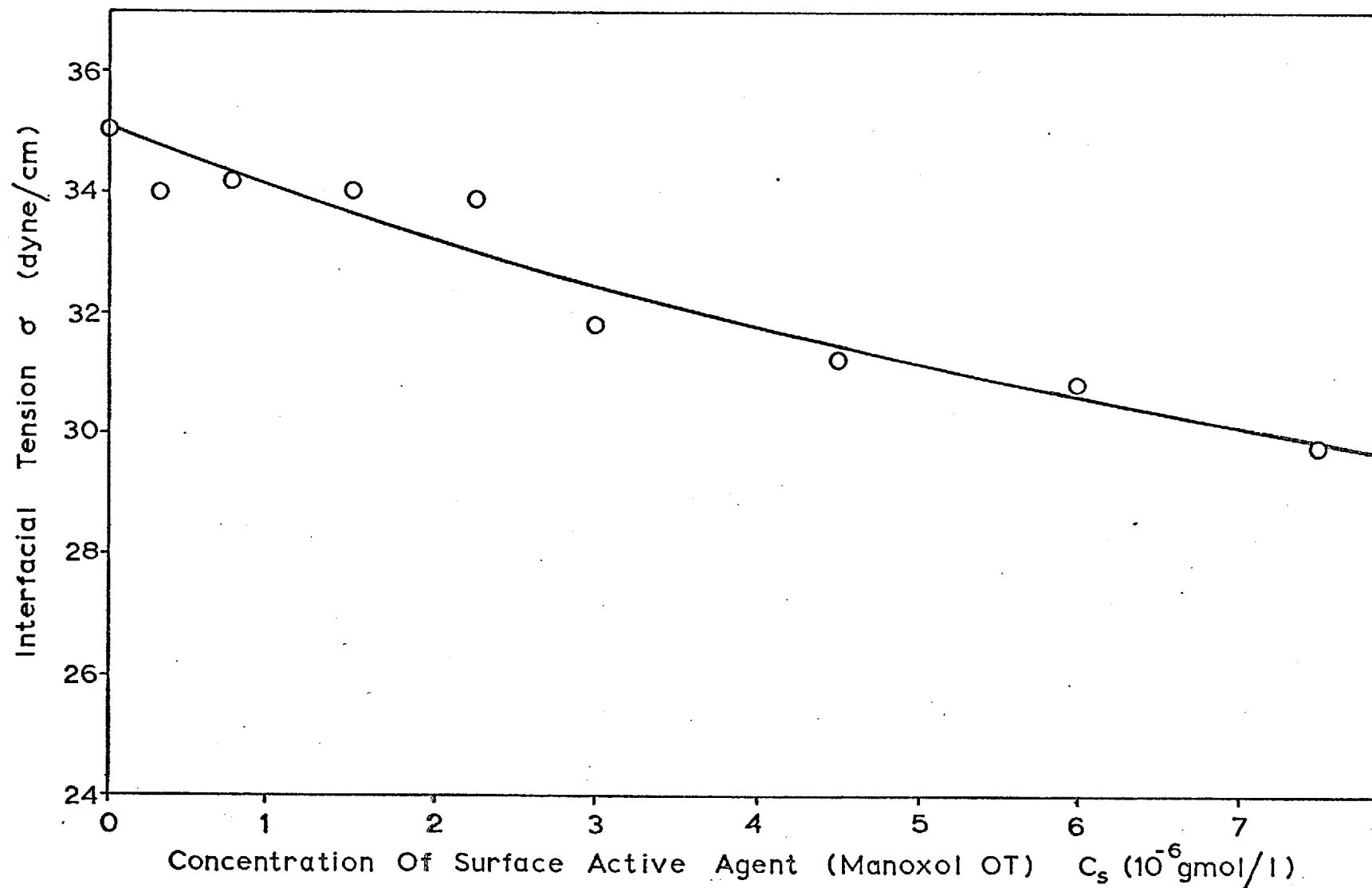


FIG.E.1: VARIATION OF INTERFACIAL TENSION WITH CONCENTRATION OF SURFACE ACTIVE AGENT MANOXOL-OT IN THE AQUEOUS PHASE

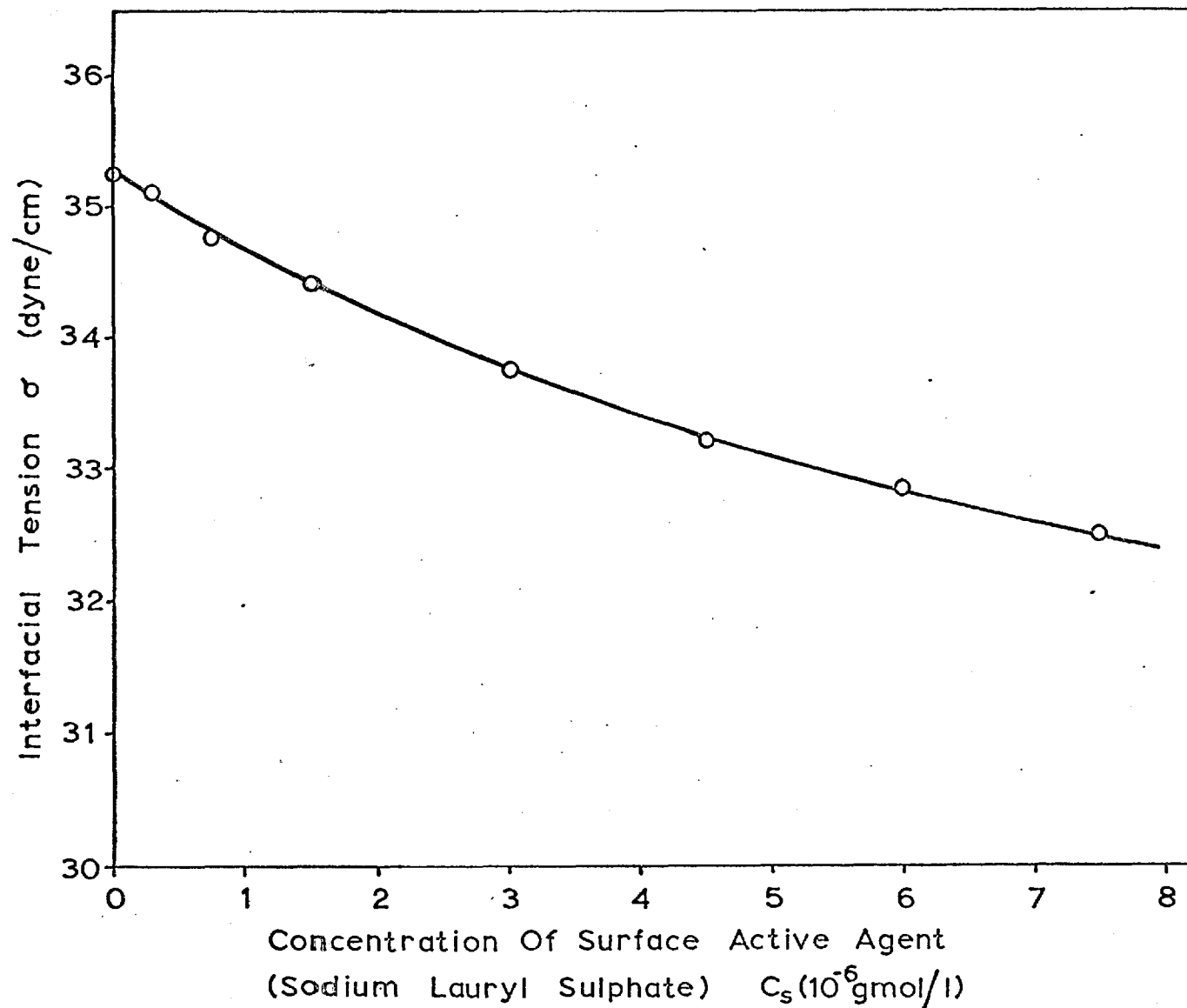


FIG.E.2 : VARIATION OF INTERFACIAL TENSION WITH CONCENTRATION OF SURFACE ACTIVE AGENT SODIUM LAURYL SULPHATE IN THE AQUEOUS PHASE

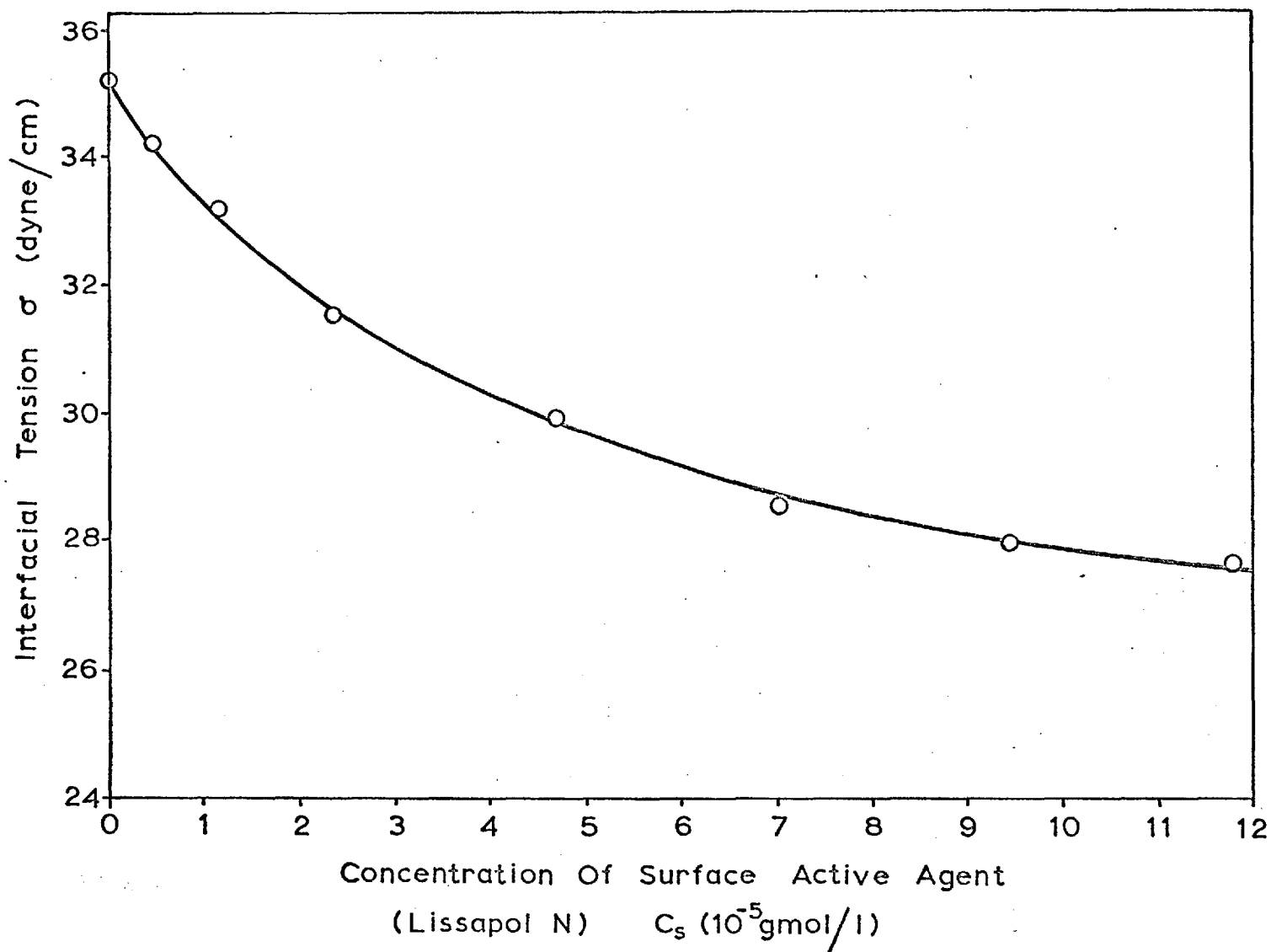


FIG.E.3: VARIATION OF INTERFACIAL TENSION WITH CONCENTRATION OF SURFACE ACTIVE AGENT LISSAPOL-N IN THE AQUEOUS PHASE

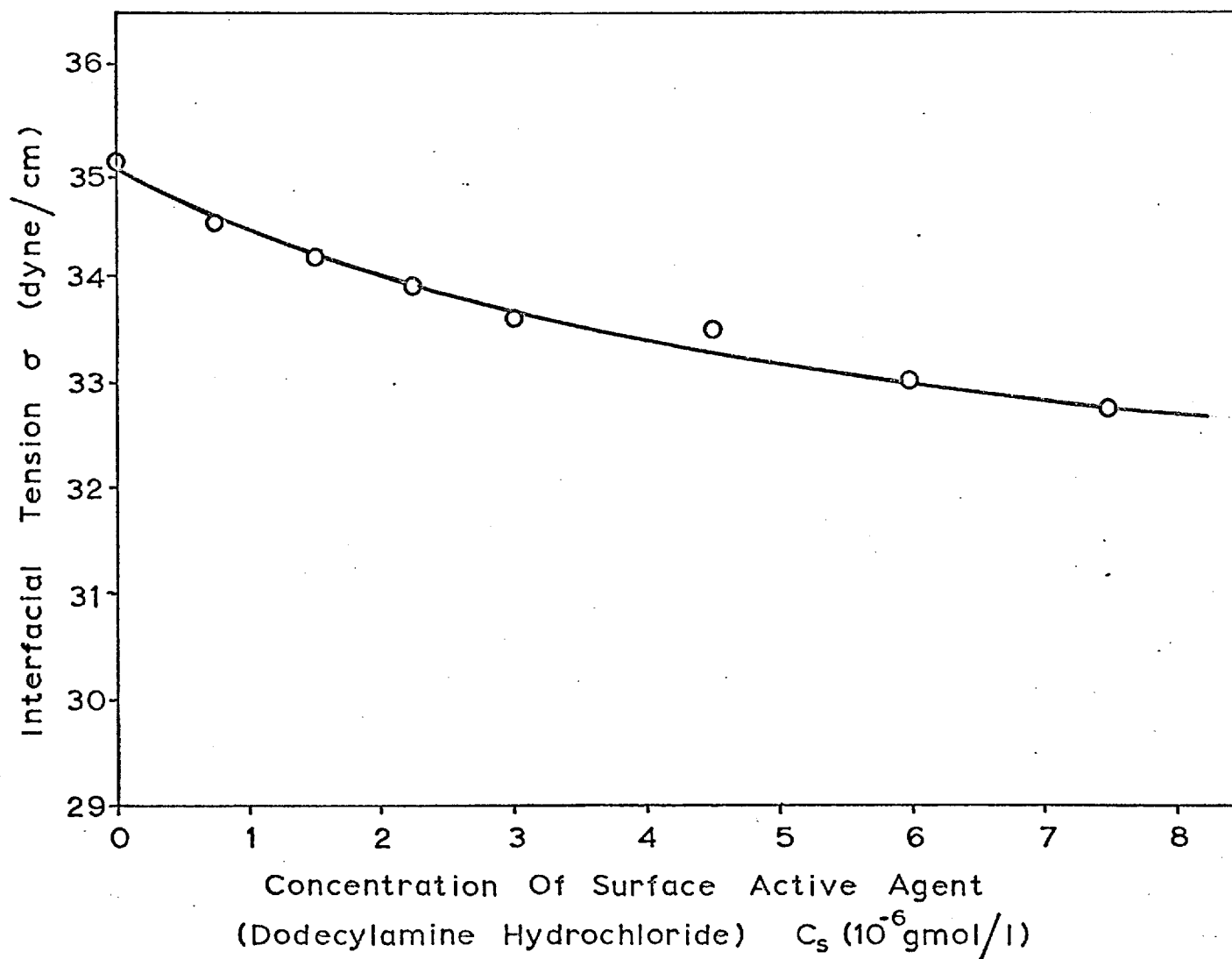


FIG. E.4: VARIATION OF INTERFACIAL TENSION WITH CONCENTRATION OF SURFACE ACTIVE AGENT DODECYLAMINE HYDROCHLORIDE IN THE AQUEOUS PHASE

APPENDIX F

Compressibility Data - Graphical Method of Evaluation

Table I - Absence of Surface Active Agents

Runs 1 - 16 ... Transfer of Acetic Acid from Benzene Drop to Water - C_B in constant at 0.487 M
 $\therefore \sigma_{Bb}^* = 12.3$ dynes/cm.

Run	C_{wb}	C_{wi}	C_{Bi}	σ_i^*	$(\sigma_i^* - \sigma_{Bb}^*)$ $= \Delta\pi$	$A_i \cdot 10^{10}$	$\frac{dA}{d(\Delta\pi)} \cdot 10^{10}$	$\frac{1}{M_i} = \frac{1}{A} \frac{dA}{d(\Delta\pi)}$	M_i
1	.000	.690	.02	27.9	15.6	249			
2	.249	.963	.031	26.2	13.9	171	- 53.4	.312	3.2
3	.459	1.172	.045	25.2	12.9	126	- 26.6	.211	4.7
4	.750	1.419	.063	23.9	11.6	100	- 17.1	.171	5.8
5	.764	1.460	.066	23.7	11.4	97.1	- 16.7	.172	5.7
6	1.019	1.700	.088	22.6	10.3	82.4	- 9.0	.109	9.2
7	1.030	1.718	.091	22.5	10.2	81.5	- 9.0	.110	9.1
8	1.264	1.934	.111	21.6	9.3	77.9	- 7.5	.096	10.4
9	1.500	2.150	.134	20.7	8.4	69.8	- 5.0	.072	13.9
10	1.509	2.160	.135	20.7	8.4	69.6	- 3.64	.052	19.3
11	1.825	2.460	.167	19.6	7.3	65.1	- 2.86	.044	22.8
12	2.103	2.720	.194	18.6	6.3	62.7	- 2.14	.034	29.4
13	2.141	2.758	.198	18.5	6.2	63.1	- 2.14	.034	29.4
14	2.645	3.223	.260	16.9	4.6	59.6	- 1.25	.021	47.6
15	2.645	3.223	.260	16.9	4.6	59.6	- 1.25	.021	47.6
16	3.145	3.69	.325	15.6	3.3	57.9	- 0.77	.013	77.0

Runs 17 - 31 ... Transfer of Acetic Acid from Benzene Drop to Water

- C_B in constant at 0.98 M

(For column heads see previous page)

$$\therefore \sigma_{Bb}^* = 8.0 \text{ dynes/cm.}$$

17	.000	1.43	.462	23.9	15.9	101.5			
18	.226	1.67	.085	22.7	14.7	83.8	- 10.6	.126	7.9
19	.426	1.85	.100	22.0	14.0	77.8	- 8.1	.104	9.6
20	.604	2.01	.120	21.3	13.3	73.3	- 6.2	.084	11.9
21	.770	2.17	.136	20.7	12.7	69.6	- 5.4	.077	13.0
22	.975	2.35	.153	20.0	12.0	66.5	- 4.0	.060	16.7
23	1.180	2.57	.179	19.2	11.2	63.9	- 2.86	.045	22.2
24	1.398	2.74	.195	18.5	10.5	62.6	- 2.2	.035	29.6
25	1.853	2.96	.223	17.8	9.8	61.2	- 1.67	.027	27.0
26	2.240	3.51	.300	16.1	8.1	58.2	- .79	.013	77.0
27	2.810	4.05	.379	14.5	6.5	57.5	- .18	.003	334.0
28	3.293	4.50	.448	13.6	5.6	57.8	0.0	.000	∞
29	3.774	4.94	.578	12.6	4.6	58.3	0.0	.000	∞
30	4.195	5.35	.589	11.7	3.7	58.5	0.0	.000	∞
31	4.763	5.85	.681	10.7	2.7	59.5	0.0	.000	∞

Runs 32 - 40 ... Transfer of Acetic Acid from Benzene Drop to Water

- C_B in constant at 1.94 M

$$\therefore \sigma_{Bb}^* = 4.2 \text{ dynes/cm}$$

32	.000	2.76	.196	18.5	14.3	63.6			
33	.510	3.28	.269	16.7	12.5	59.0	- 1.25	.021	47.6
34	1.112	3.69	.325	15.6	11.4	57.9	- .42	.007	14.3
35	1.603	4.23	.403	14.2	10.0	57.6	0.0	.000	∞
36	2.205	4.76	.489	13.0	8.8	57.9	0.0	.000	∞
37	2.617	4.94	.519	12.6	8.4	58.4	0.0	.000	∞
38	3.720	6.21	.753	9.9	5.7	58.8	0.0	.000	∞
39	4.234	6.71	.871	9.0	4.8	59.5	0.0	.000	∞
40	4.753	7.2	.997	8.2	4.0	57.0	0.0	.000	∞

Runs 143 - 153 ... Transfer of Acetic Acid from Water to Benzene Drop - $C_B = 0$

Run	C_{wb}	C_{wi}	σ_{wb}^*	σ_i^*	$(\sigma_i^* - \sigma_{wb}^*)$ $= \Delta\pi$	$A_i \cdot 10^{10}$	$\frac{dA}{d(\Delta\pi)} 10^{10}$	$\frac{1}{M_i} = -\frac{1}{A} \frac{dA}{d(\Delta\pi)}$	M_i
143	.000	.000	37.5	37.5	0.0	∞	-	∞	0.0
144	.030	.0015	33.5	36.5	3.0	408	- 100	.246	4.06
145	.058	.0141	30.3	35.4	5.1	222	- 45	.203	4.93
146	.060	.0147	30.0	35.4	5.4	214	- 42	.196	5.1
147	.115	.0263	24.5	33.8	9.3	125	- 14.6	.117	8.55
148	.150	.0335	21.4	33.0	11.6	94.6	- 9.25	.097	10.3
149	.173	.0384	19.5	32.4	12.9	89.9	- 8.0	.089	11.2
150	.230	.0505	15.4	30.9	15.3	71.5	- 6.0	.084	11.9
151	.250	.0550	14.3	30.5	16.2	66.7	- 5.61	.084	11.9
152	.288	.0630	12.0	29.5	17.5	60.0	- 5.22	.087	11.5
153	.345	.0725	9.1	28.5	19.4	54.1	- 4.61	.085	11.8

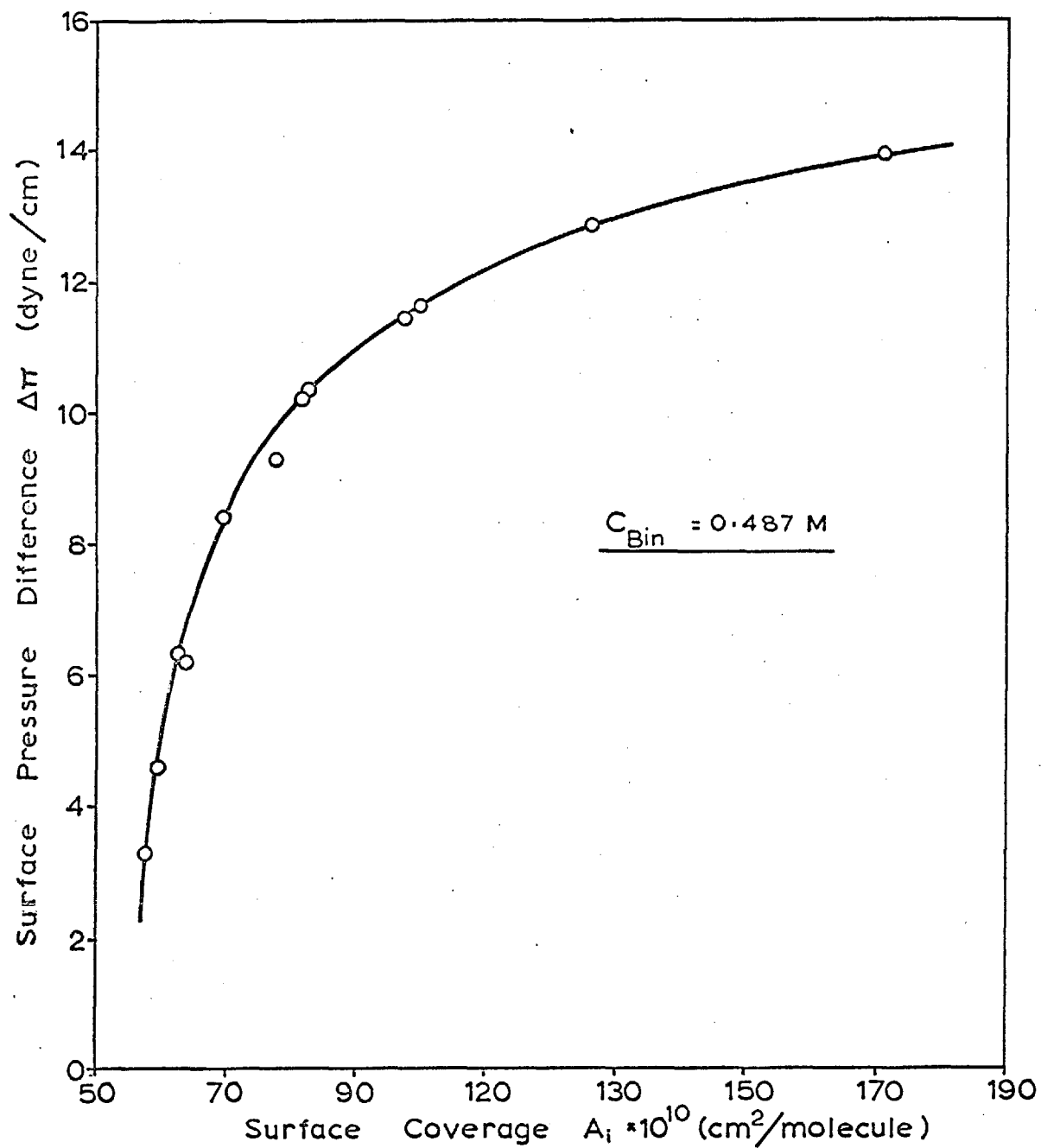


FIG. F.1: $\Delta\pi$ -A PLOT FOR THE TRANSFER OF ACETIC ACID FROM BENZENE TO WATER

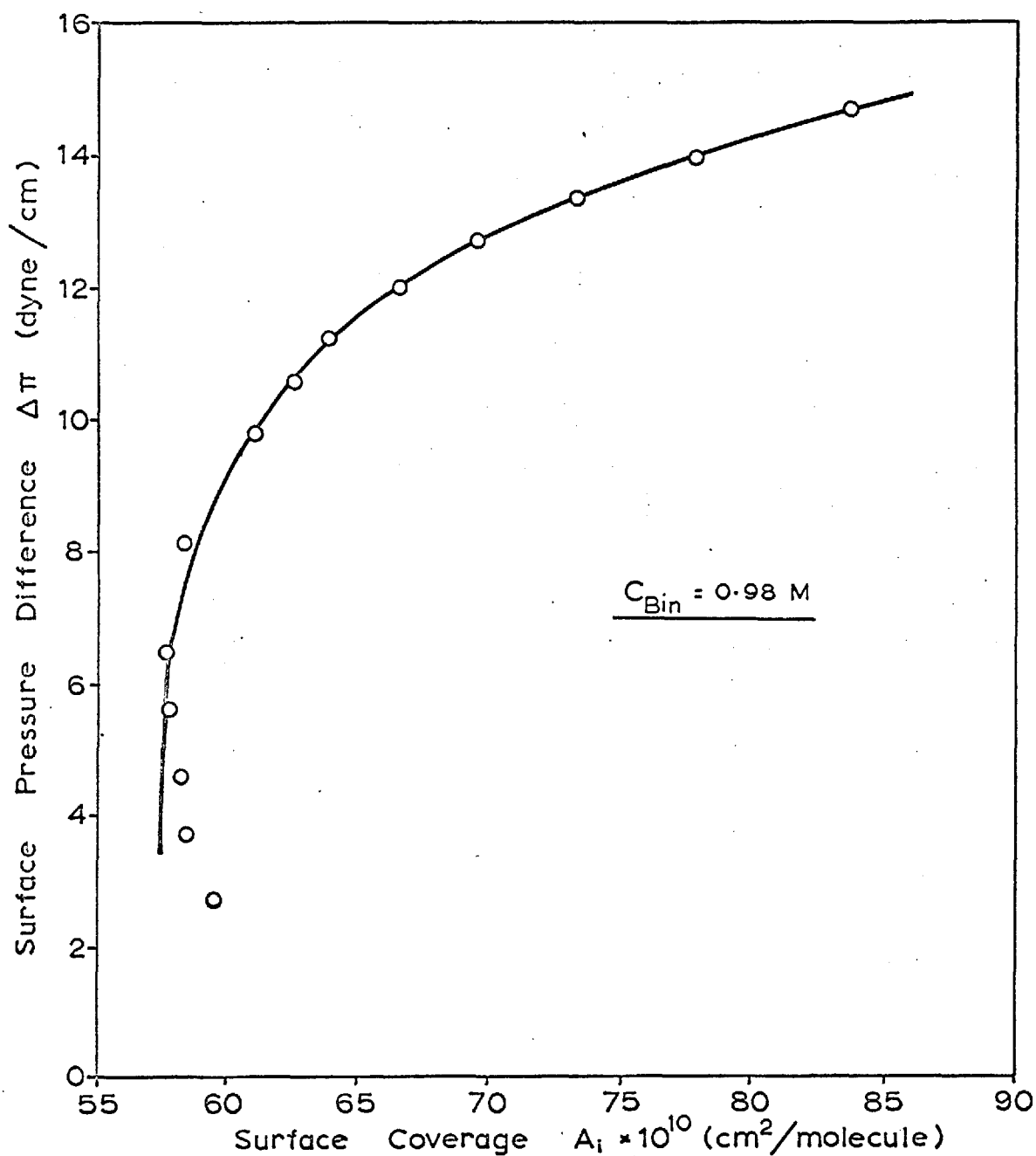


FIG. F.2 : $\Delta\pi$ -A PLOT FOR THE TRANSFER OF ACETIC ACID FROM BENZENE TO WATER

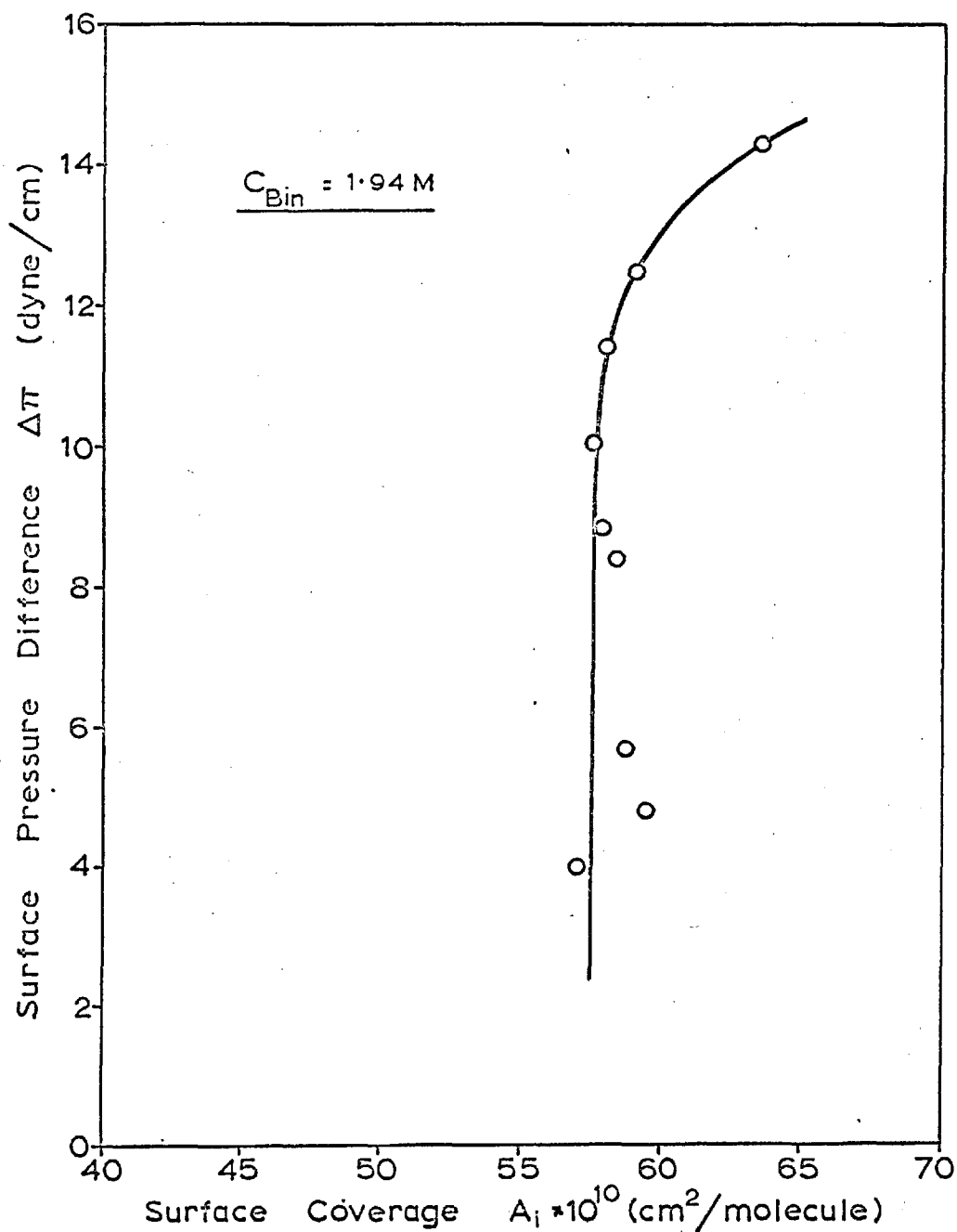


FIG. F.3: $\Delta\pi$ -A PLOT FOR THE TRANSFER OF ACETIC ACID FROM BENZENE TO WATER

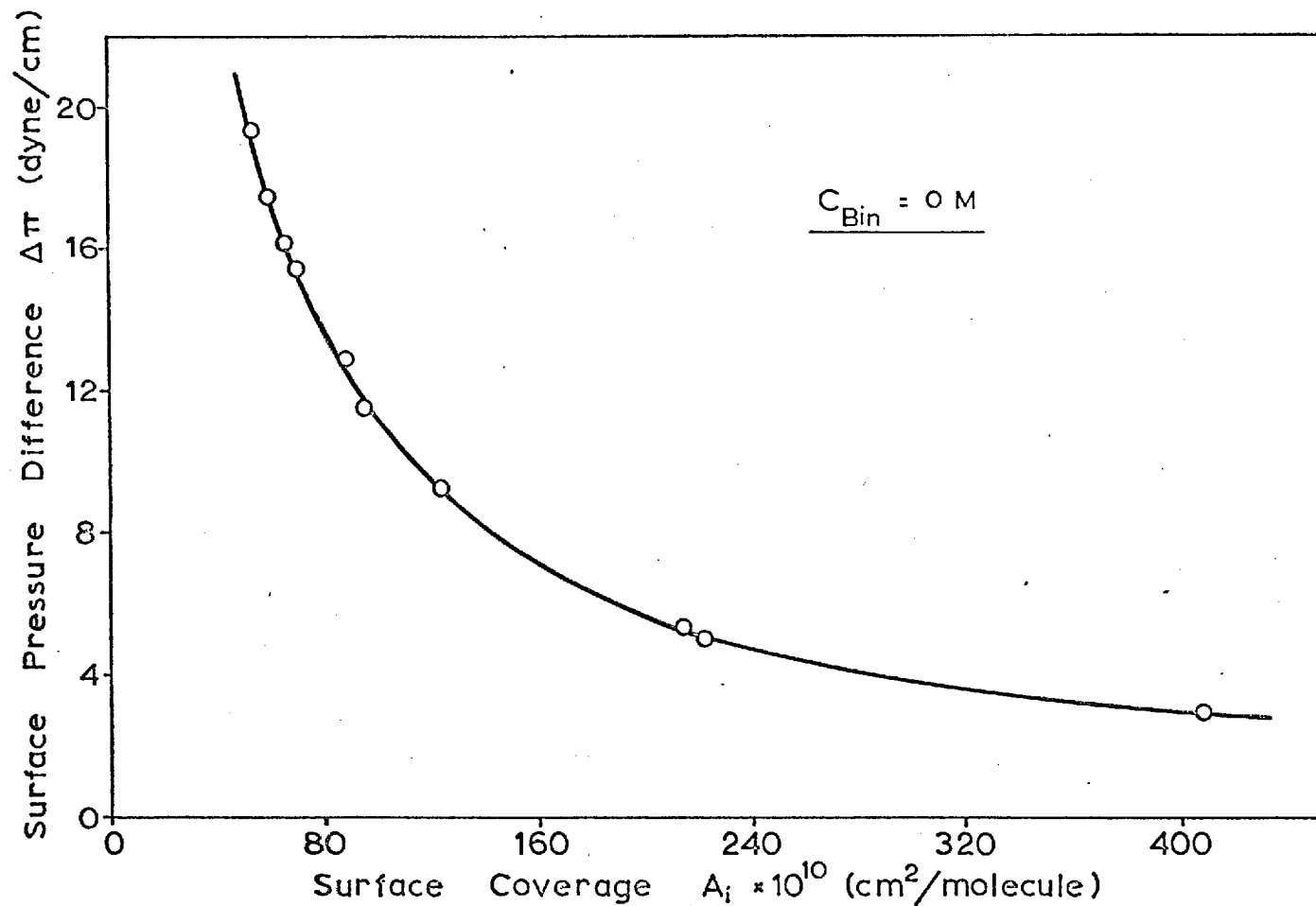


FIG. F.4 $\Delta\pi - A$ PLOT FOR THE TRANSFER OF PHENOL
FROM WATER TO BENZENE

Table II - Presence of Surface Active Agents

Of the five surface active agents tabulated below, in each case the transfer was of acetic acid from a benzene drop to water, with $C_w = 0$ and $C_{B \text{ in}} = 0.980$

Runs 44 - 51 ... Surface active agent - Dodecylamine Hydrochloride

Run	$C_s \cdot 10^6$	C^*	$\pi = (\sigma_o - \sigma^*)$	$A \cdot 10^{13}$	$\frac{d\pi}{dA} \cdot 10^{13}$	$M = -A \frac{d\pi}{dA}$	M^{-1}
44	0.0	34.94	0.0	∞		0.0	∞
45	.75	34.56	.38	1.28	- .24	.31	3.2
46	1.5	34.27	.67	.755	- .91	.69	1.45
47	2.25	34.00	.94	.519	- 1.87	.97	1.03
48	3.0	33.78	1.16	.404	- 3.2	1.29	.77
49	4.5	33.36	1.58	.33	- 6.6	2.18	.46
50	6.0	33.00	1.94	.279	- 8.6	2.4	.42
51	7.5	32.75	2.19	.264	- 12.0	3.17	.31

Runs 68 - 76 ... Surface active agent - Teepol 514

68	0.0	35.1	0.0	∞		0.0	∞
69	9.1	34.0	1.1	.44	- 2.2	.97	1.03
70	27.8	32.7	2.4	.198	- 8.4	1.66	0.6
71	45.6	30.7	4.4	.108	- 44.0	4.73	.21
72	68.5	29.0	6.1	.083	- 107.0	8.9	.11
73	91.3	27.4	7.7	.069	- 170.0	11.6	.086
74	136.9	24.8	10.3	.055	- 220.0	12.1	.083
75	182.5	22.7	12.4	.055	- 220.0	12.1	.083
76	228.2	21.3	13.8	.063	- 320.0	20.0	.050

Runs 104 - 112 ... Surface active agent - Manoxol OT

(For column heads see previous page)

104	0.0	35.1	0.0	∞		0.0	∞
105	0.3	34.72	.38	1.43	- .26	.37	2.7
106	0.75	34.3	.8	.62	- .98	.61	1.64
107	1.5	33.64	1.46	.32	- 4.6	1.47	.68
108	2.25	33.01	2.09	.23	- 10.5	2.43	.41
109	3.0	32.45	2.65	.194	- 15.0	2.91	.32
110	4.5	31.5	3.6	.149	- 28.5	4.16	.24
111	6.0	30.64	4.46	.132	- 38.0	5.01	.20
112	7.5	29.9	5.2	.12	- 50.7	6.1	.16

Runs 113 - 121 ... Surface active agent - Sodium Lauryl Sulphate

113	0.0	35.27	0.0	∞		0.0	∞
114	.3	35.05	.22	2.3	- .214	.49	2.02
115	.75	34.81	.46	.99	- .39	.39	2.56
116	1.5	34.41	.86	.551	- 1.92	1.06	.94
118	3.0	33.75	1.52	.365	- 5.57	2.04	.49
119	4.5	33.73	2.04	.306	- 9.0	2.76	.36
120	6.0	32.84	2.43	.288	- 12.5	3.6	.28
121	7.5	32.47	2.8	.257	- 18.0	4.63	.22

Runs 122 - 130 ... Surface active agent - Lissapol N

122	0.0	35.2	0.0			0.0	∞
123	4.71	34.25	0.95	.526	- 1.11	.584	1.71
124	11.79	33.2	2.0	.252	- 8.9	2.24	.45
125	23.55	31.7	3.5	.172	- 57.5	9.9	.101
127	47.1	29.75	5.45	.148	- 100.	14.8	.068
128	70.65	28.6	6.6	.145	- 100.	14.5	.069
129	94.2	27.98	7.22	.194	- 282.	5.46	18.0
130	117.9	27.6	7.6	.247	- 93.	23.0	.043

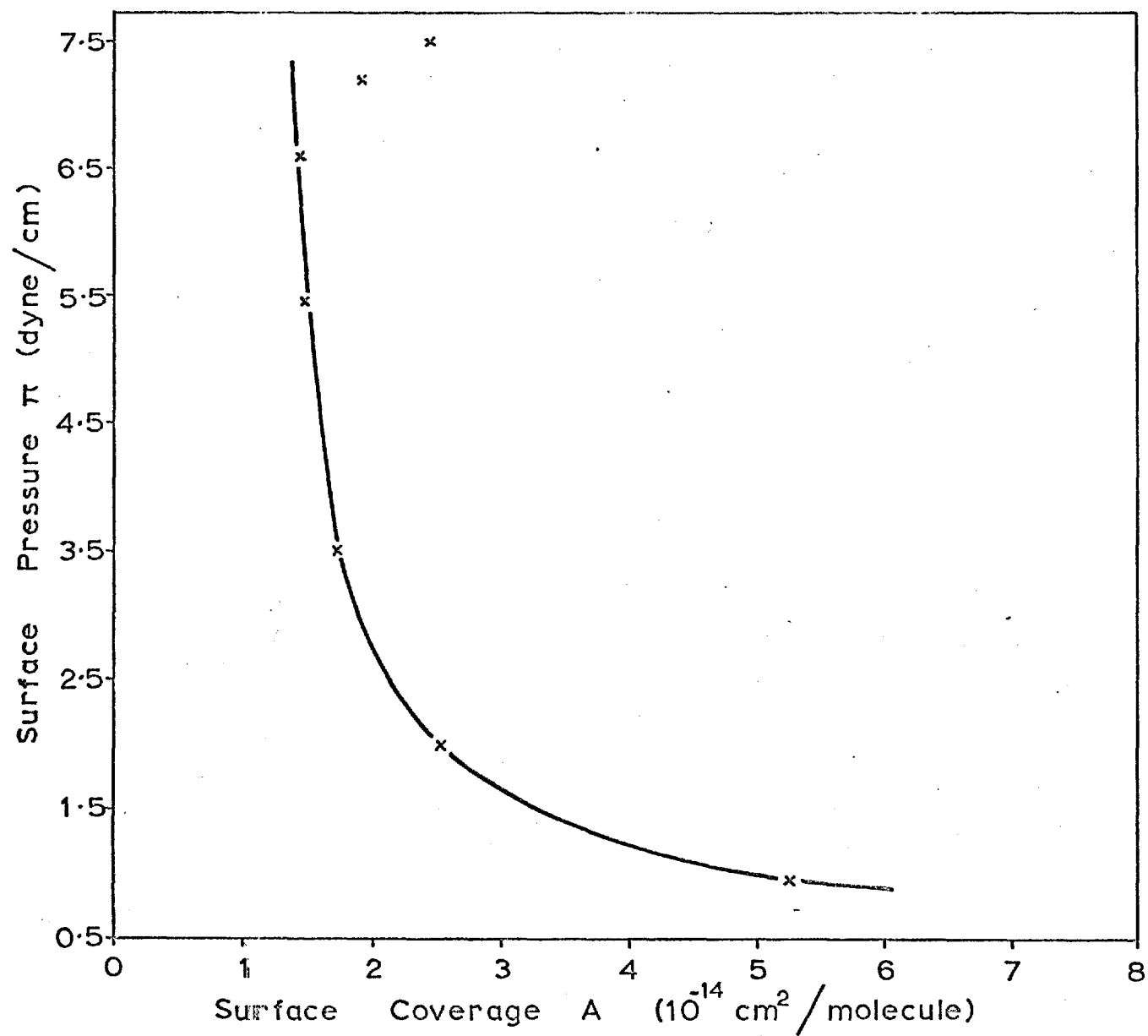


FIG. F.5 : π - A PLOT FOR SURFACE ACTIVE AGENT LISSAPOL N

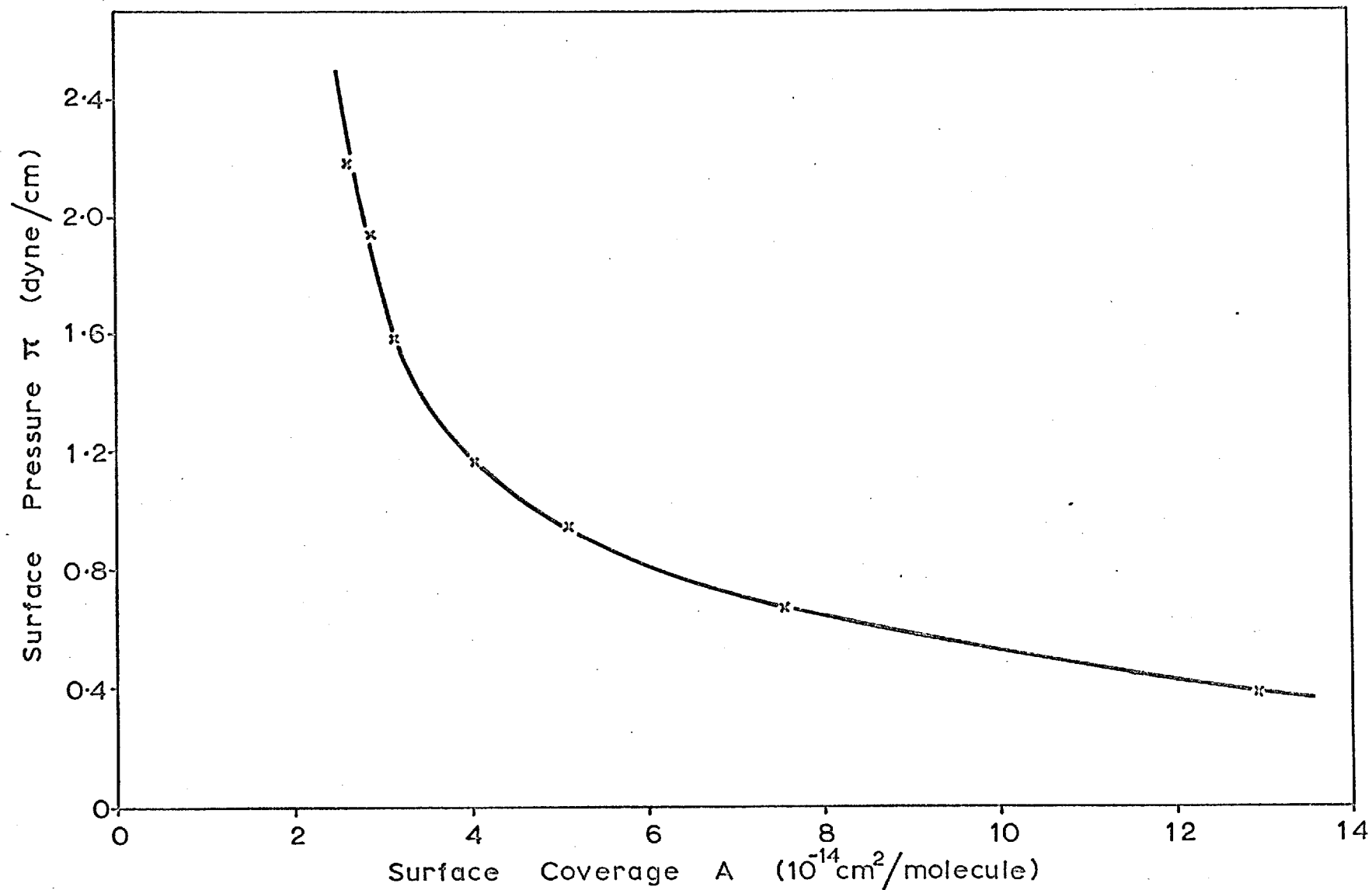


FIG. F.6 : π -A PLOT FOR SURFACE ACTIVE AGENT DODECYLAMINE HYDROCHLORIDE

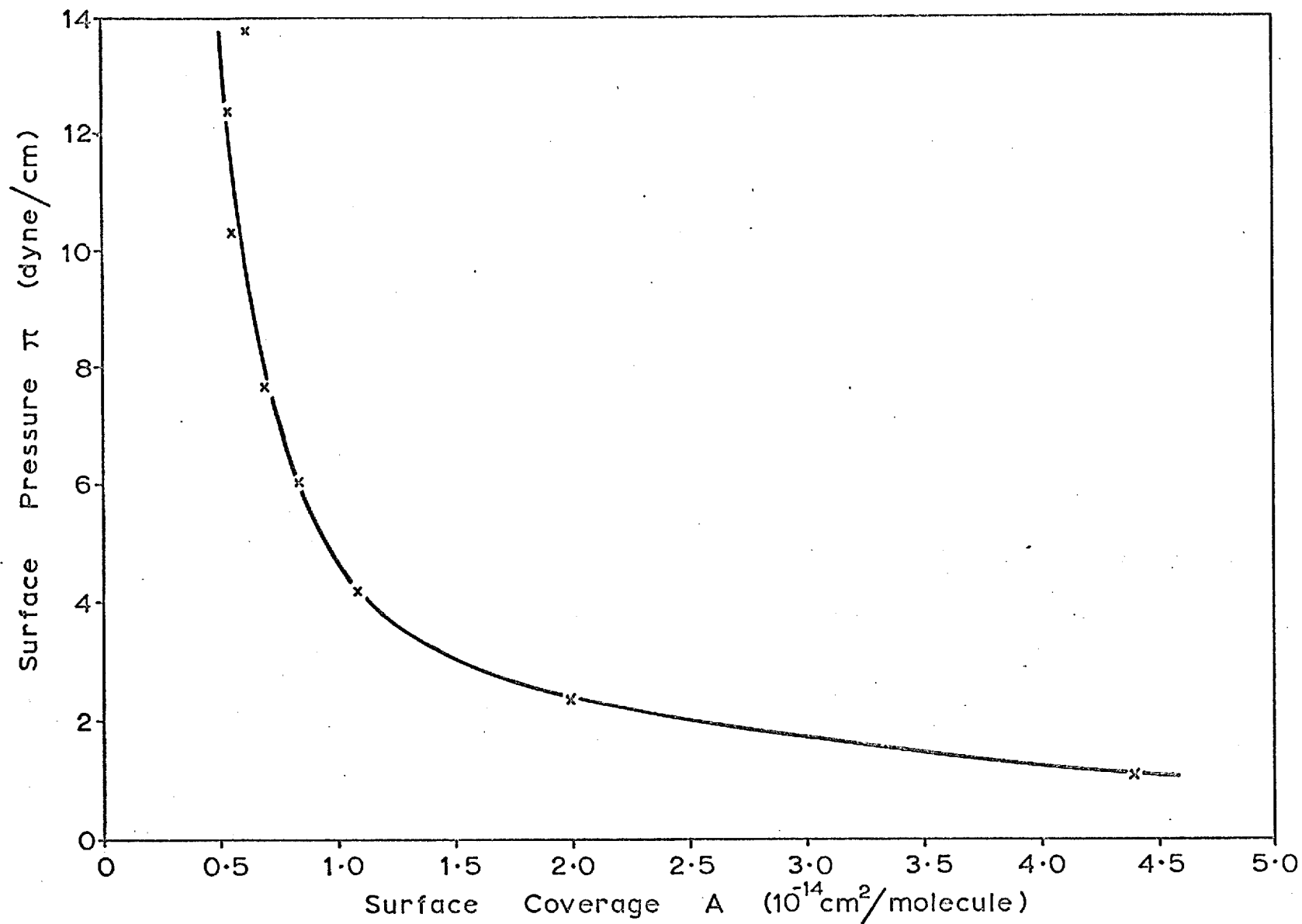


FIG. F.7: π - A PLOT FOR SURFACE ACTIVE AGENT TEEPOL 514

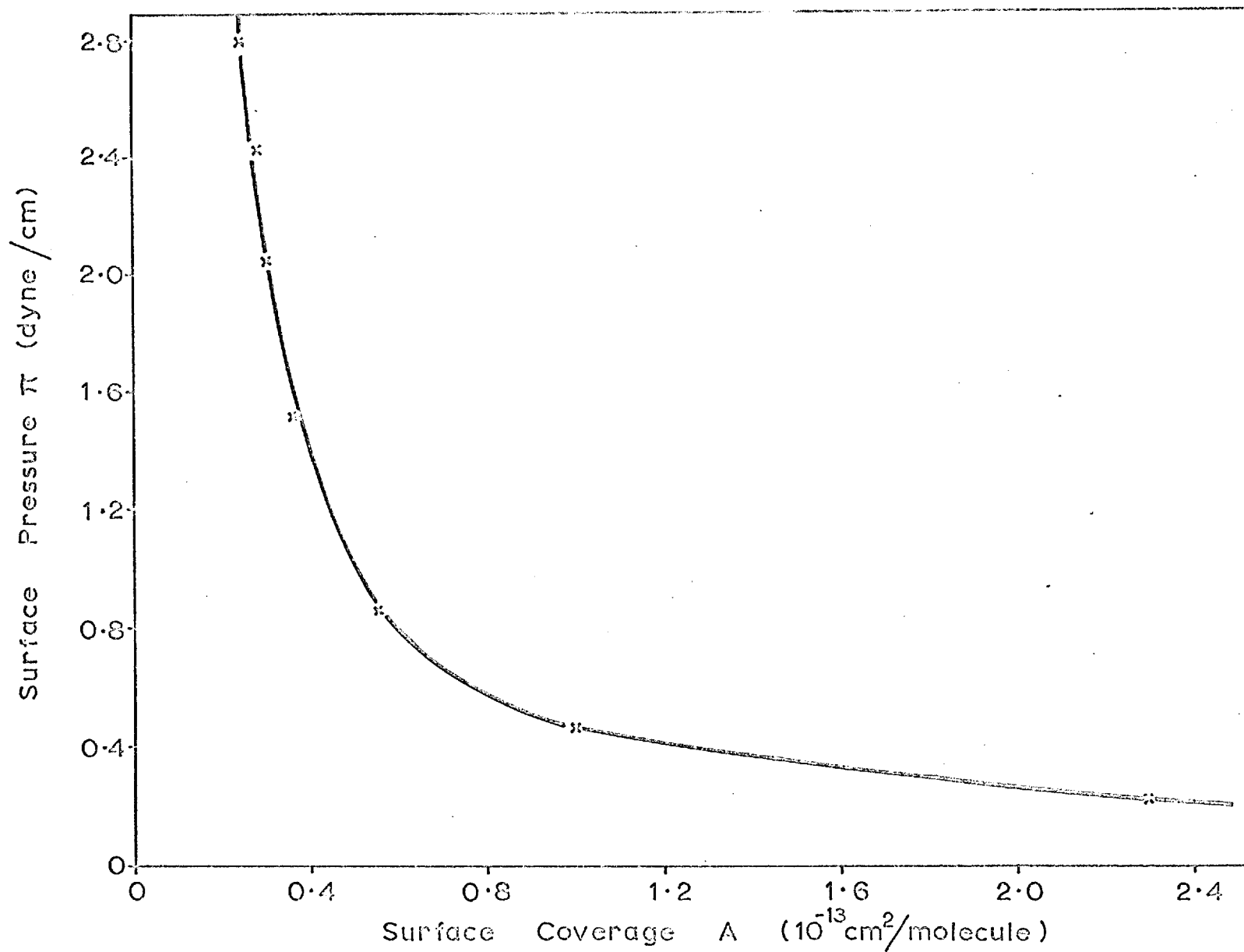


FIG. F.8 : π - A PLOT FOR SURFACE ACTIVE AGENT SODIUM LAURYL SULPHATE

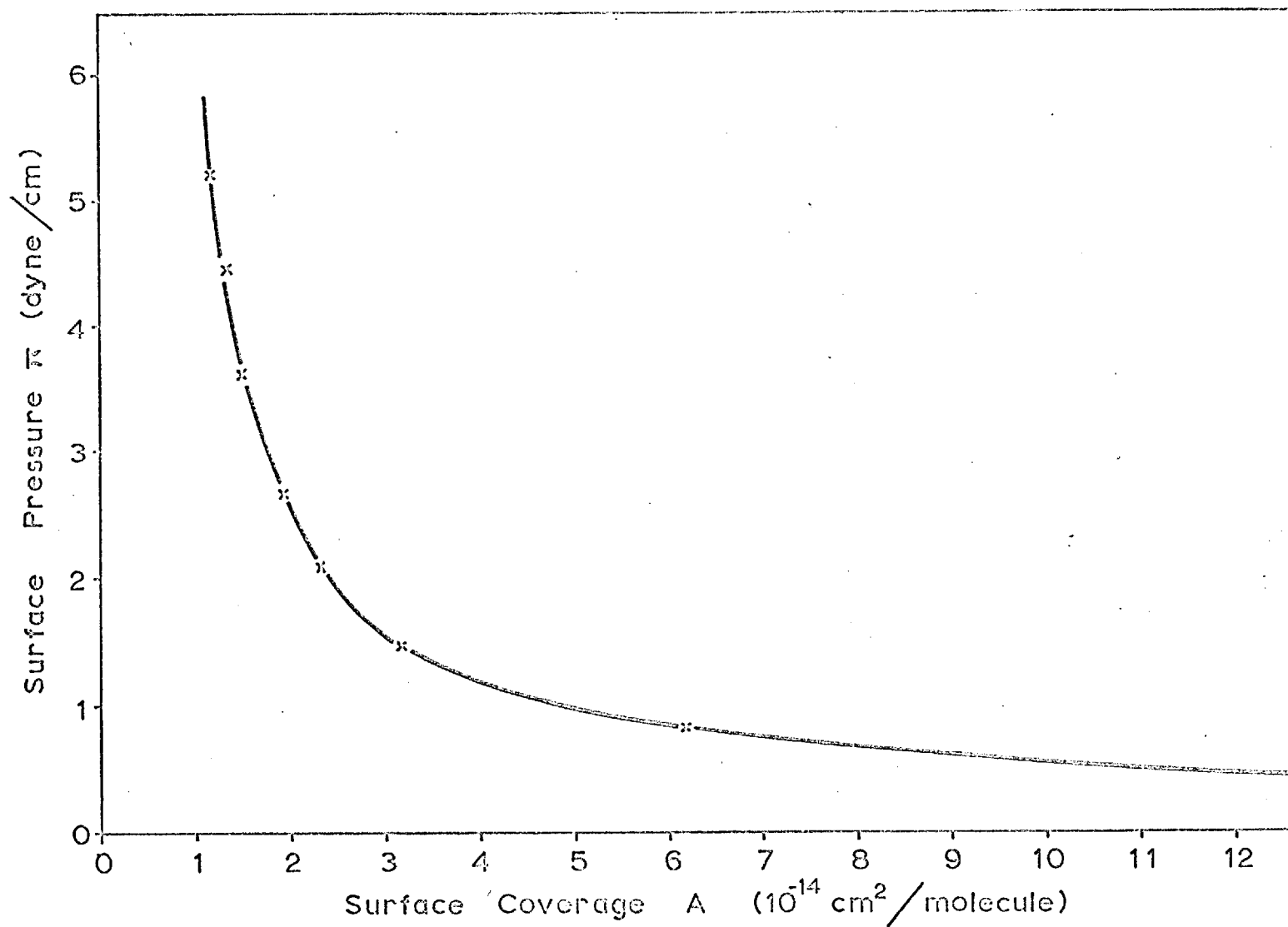


FIG. F.9 : π -A PLOT FOR SURFACE ACTIVE AGENT MANOXOL OT

APPENDIX G

Compressibility Data - Numerical Method of Evaluation

Table I - Absence of Surface Active Agents

Runs 1 - 16 ... Transfer of Acetic Acid from Benzene Drop to Water - C_B in constant at 0.487 M
 $\therefore \sigma_{Bb}^* = 12.3$ dynes/cm.

Run	C_w	C_{Bi}	σ_i^*	$\Delta\pi = (\sigma_i^* - \sigma_{Bb}^*)$	$\log C_{Bi}$	n	M_i	K_i^{-1}
1	0.0	.02	27.9	15.6	- 1.7	- 8.1	5.35	.187
2	.249	.031	26.2	13.9	- 1.51	- 8.1	6.31	.159
3	.459	.045	25.2	12.9	- 1.35	- 8.1	6.86	.146
4	.750	.063	23.9	11.6	- 1.20	- 8.1	7.23	.138
5	.764	.066	23.7	11.4	- 1.18	- 8.1	7.25	.138
6	1.019	.088	22.6	10.3	- 1.06	- 8.1	8.72	.115
7	1.030	.091	22.5	10.2	- 1.04	- 8.1	8.70	.115
8	1.264	.111	21.6	9.3	- 0.95	- 13.6	12.2	.082
9	1.500	.134	20.7	8.4	- 0.87	- 13.6	12.4	.081
10	1.509	.135	20.7	8.4	- 0.87	- 13.6	12.5	.080
11	1.825	.167	19.6	7.3	- 0.78	- 13.6	12.7	.079
12	2.103	.194	18.6	6.3	- 0.71	- 13.6	12.8	.078
13	2.141	.198	18.5	6.2	- 0.70	- 13.6	12.8	.078
14	2.645	.260	16.9	4.6	- 0.59	- 13.6	13.0	.077
15	2.645	.260	16.9	4.6	- 0.59	- 13.6	13.0	.077
16	3.145	.325	15.6	3.3	- 0.49	- 13.6	13.1	.076

Runs 17 - 31 ... Transfer of Acetic Acid from Benzene Drop to Water - C_B in constant at 0.980 M
 (For column heads see previous page) $\therefore \sigma_{Bb}^* = 8.0 \text{ dynes/cm}$

17	0.0	.062	23.9	15.9	- 1.21	- 11.1	9.45	.106
18	.226	.085	22.7	14.7	- 1.07	- 11.1	11.2	.089
19	.426	.100	22.0	14.0	- 1.00	- 11.1	11.5	.087
20	.604	.120	21.3	13.3	- 0.92	- 11.1	11.6	.086
21	.770	.136	20.7	12.7	- 0.87	- 11.1	11.7	.085
22	.975	.153	20.6	12.0	- 0.82	- 11.1	11.8	.085
23	1.180	.179	19.2	11.2	- 0.75	- 11.1	11.9	.084
24	1.398	.195	18.5	10.5	- 0.71	- 14.15	11.6	.086
25	1.853	.223	17.8	9.8	- 0.65	- 14.15	11.7	.085
26	2.240	.300	16.1	8.1	- 0.52	- 14.15	11.9	.084
27	2.810	.379	14.5	6.5	- 0.42	- 14.15	12.1	.083
28	3.293	.488	13.6	5.6	- 0.35	- 14.15	12.1	.083
29	3.774	.518	12.6	4.6	- 0.29	- 14.15	12.2	.082
30	4.195	.589	11.7	3.7	- 0.23	- 14.15	12.2	.082
31	4.763	.681	10.7	2.7	- 0.17	- 14.15	12.2	.082

Runs 32 - 40 ... Transfer of Acetic Acid from Benzene Drop to Water - C_B in constant at 1.94 M
 $\therefore \sigma_{Bb}^* = 4.2 \text{ dynes/cm}$

32	0.0	.196	18.5	14.3	- 0.71	- 15.3	14.3	.070
33	.510	.269	16.7	12.5	- 0.57	- 15.3	14.5	.069
34	1.112	.325	15.6	11.4	- 0.488	- 15.3	14.7	.068
35	1.603	.403	14.2	10.0	- 0.395	- 15.3	14.8	.068
36	2.205	.489	13.0	8.8	- 0.311	- 15.3	14.9	.067
37	2.617	.519	12.6	8.4	- 0.285	- 15.3	14.9	.067
38	3.720	.753	9.9	5.7	- 0.123	- 15.3	15.0	.067
39	4.234	.871	9.0	4.8	- 0.06	- 15.3	15.0	.067
40	4.753	.997	8.2	4.0	- 0.001	- 15.3	15.0	.067

Runs 143 - 153 ... Transfer of Acetic Acid from Water to Benzene Drop - $C_{B \text{ in}}$ constant at 0.0 M

Run	C_w	C_{wi}	σ_{wb}^*	σ_i^*	$\Delta\pi = \sigma_i^* - \sigma_{wb}^*$	$\log C_{wi}$	$\log \Delta\pi$	n	$\log \alpha$	$\log M_i$	M_i	M_i^{-1}
143	.000	.000	37.5	37.5	0.0	- ∞				- ∞	0.0	∞
144	.030	.0075	33.5	36.5	3.0	- 2.125	.477	.894	2.38	.480	3.02	.330
145	.058	.0141	30.3	35.4	5.1	- 1.851	.707	.894	2.38	.728	5.34	.187
146	.060	.0147	30.0	35.4	5.4	- 1.863	.732	.894	2.38	.716	5.20	.192
147	.115	.0263	24.5	33.8	9.3	- 1.580	.968	.894	2.38	.969	9.31	.107
148	.150	.0335	21.4	33.0	11.6	- 1.475	1.064	.894	2.38	1.061	12.80	.078
149	.173	.0384	19.5	32.4	12.9	- 1.416	1.111	.894	2.38	1.117	12.9	.077
150	.230	.0505	15.4	30.9	15.5	- 1.297	1.190	.600	1.968	1.189	13.2	.076
151	.250	.055	14.3	30.5	16.2	- 1.260	1.209	.600	1.968	1.213	13.2	.076
152	.288	.063	12.0	29.5	17.5	- 1.201	1.243	.600	1.968	1.247	13.3	.075
153	.345	.073	9.1	28.5	19.4	- 1.140	1.258	.600	1.968	1.284	13.4	.075

Table II - Presence of Surface Active Agents

Of each of the five surface active agents tabulated below, in each case the transfer was of acetic acid from a benzene drop to water, with $C_w = 0$ and $C_{B \text{ in}} = 0.980 \text{ M}$.

Runs 44 - 51 ... Surface active agent - Dodecylamine Hydrochloride

Run	$C_s \cdot 10^6$	σ^*	π	$\log \pi$	$\log C_s$	n	$\log \alpha$	$\log M$	M	M^{-1}
44	0.0	34.94	0.0	- ∞	- ∞			- ∞	0.0	∞
45	0.75	34.56	.38	- .42	- 6.45	.81	4.54	- .42	.38	2.64
46	1.5	34.27	.67	- .174	- 5.824	.81	4.54	- .18	.66	1.52
47	2.25	34.00	.94	- .027	- 5.648	.81	4.54	- .03	.93	1.08
48	3.0	33.78	1.16	- .064	- 5.523	.81	4.54	.04	1.10	.91
49	4.5	33.36	1.58	.199	- 5.347	.59	3.35	.19	1.55	.64
50	6.0	33.00	1.94	.288	- 5.222	.59	3.35	.26	1.82	.55
51	7.5	32.75	2.19	.340	- 5.125	.59	3.35	.32	2.09	.48

Runs 68 - 76 ... Surface active agent - Teepol 514.

Run	$C_s \cdot 10^{-6}$	σ^*	π	$\log \pi$	$\log C_s$	n	$\log \alpha$	$\log M$	M	M^{-1}
68	0.0	35.1	0.0	- ∞	- ∞			- ∞	0.0	∞
69	9.1	34.0	1.1	.041	- 5.04	.833	4.23	.14	1.10	.91
70	22.8	32.7	2.4	.380	- 4.642	.833	4.23	.37	2.34	.43
71	45.6	30.7	4.4	.643	- 4.341	.833	4.23	.62	4.17	.24
72	68.5	29.0	6.1	.785	- 4.165	.833	4.23	.75	5.62	.178
73	91.3	27.4	7.7	.886	- 4.040	.833	4.23	.87	7.41	.135
74	136.9	24.8	10.3	1.013	- 3.864	.609	3.36	1.00	10.0	.100
75	182.5	22.7	12.4	1.093	- 3.739	.609	3.36	1.08	12.02	.083
76	228.2	21.3	13.8	1.14	- 3.642	.609	3.36	1.20	15.85	.063

Runs 104 - 112 ... Surface active agent - Manoxol OT

104	0.0	35.1	0.0	- ∞	- ∞			- ∞	0.0	∞
105	0.3	34.72	0.38	- .42	- 6.523	.841	5.07	- .42	.38	2.64
106	0.75	34.3	0.8	- .097	- 6.125	.841	5.07	- .08	.83	1.21
107	1.5	33.64	1.46	.164	- 5.824	.841	5.07	.17	1.48	.67
108	2.25	33.01	2.09	.320	- 5.648	.841	5.07	.32	2.09	.48
109	3.0	32.45	2.65	.423	- 5.523	.841	5.07	.42	2.63	.38
110	4.5	31.5	3.6	.556	- 5.347	.714	4.36	.55	3.55	.28
111	6.0	30.64	4.46	.649	- 5.222	.714	4.36	.63	4.27	.23
112	7.5	29.9	5.2	.716	- 5.125	.714	4.36	.70	5.01	.20

Runs 113 - 121 ... Surface active agent - Sodium Lauryl Sulphate

113	0.0	35.27	0.0	- ∞	- ∞			- ∞	0.0	∞
114	.3	35.05	.22	.658	- 6.523	.833	4.78	- .65	.22	4.55
115	.75	34.81	.46	- .337	- 6.125	.833	4.78	- .32	.48	2.08
116	1.5	34.41	.86	- .066	- 5.824	.833	4.78	.07	.85	1.18
118	3.0	33.75	1.52	.182	- 5.523	.833	4.78	.24	1.74	.57
119	4.5	33.73	2.04	.310	- 5.347	.574	3.36	.30	2.00	.50
120	6.0	32.84	2.43	.386	- 5.222	.574	3.36	.36	2.29	.44
121	7.5	32.47	2.8	.447	- 5.125	.574	3.36	.42	2.63	.38

Runs 122 - 130 ... Surface active agent - Lissapol N

Run	$C_s \cdot 10^{-6}$	σ^*	π	$\log \pi$	$\log C_s$	n	$\log \alpha$	$\log M$	M	M^{-1}
122	0.0	35.2	0.0	- ∞	- ∞			- ∞	0.0	∞
123	4.71	34.25	.95	- .022	- 5.318	0.8	4.25	- .01	.98	1.02
124	11.79	33.2	2.0	.301	- 4.929	0.8	4.25	.31	2.04	.49
125	23.55	31.7	3.5	.544	- 4.628	0.8	4.25	.55	3.55	.28
127	47.1	29.75	5.45	.736	- 4.327	0.8	4.25	.79	6.16	.20
128	70.65	28.6	6.6	.820	- 4.151	0.24	1.819	.823	6.65	.15
129	94.2	27.98	7.22	.854	- 4.026	0.24	1.819	.853	7.13	.14
130	117.9	27.6	7.6	.881	- 3.929	0.24	1.819	.875	7.50	.13

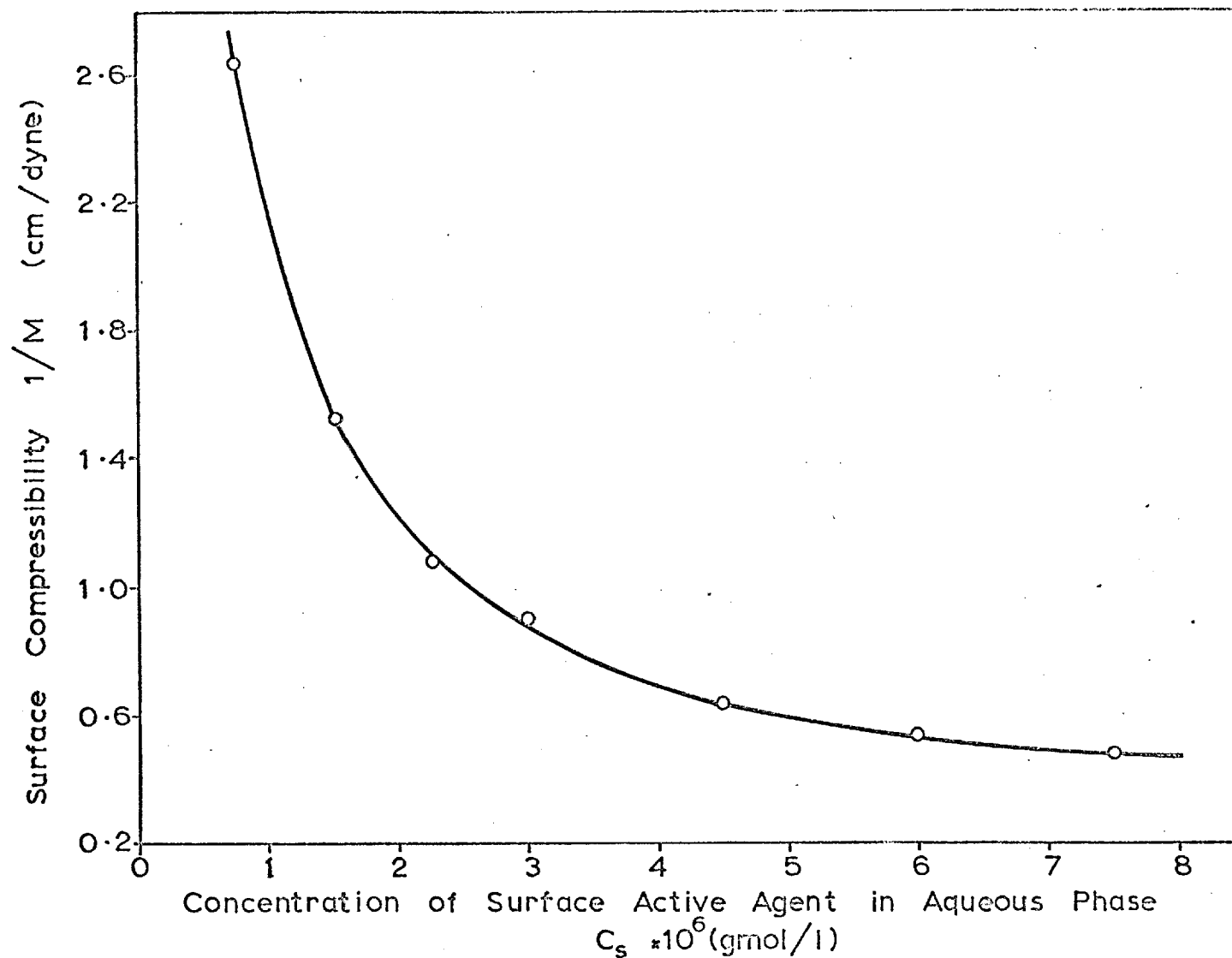


FIG. G.1: SURFACE COMPRESSIBILITY AS A FUNCTION OF THE CONCENTRATION OF SURFACE ACTIVE AGENT DODECYLAMINE HYDROCHLORIDE IN THE AQUEOUS PHASE

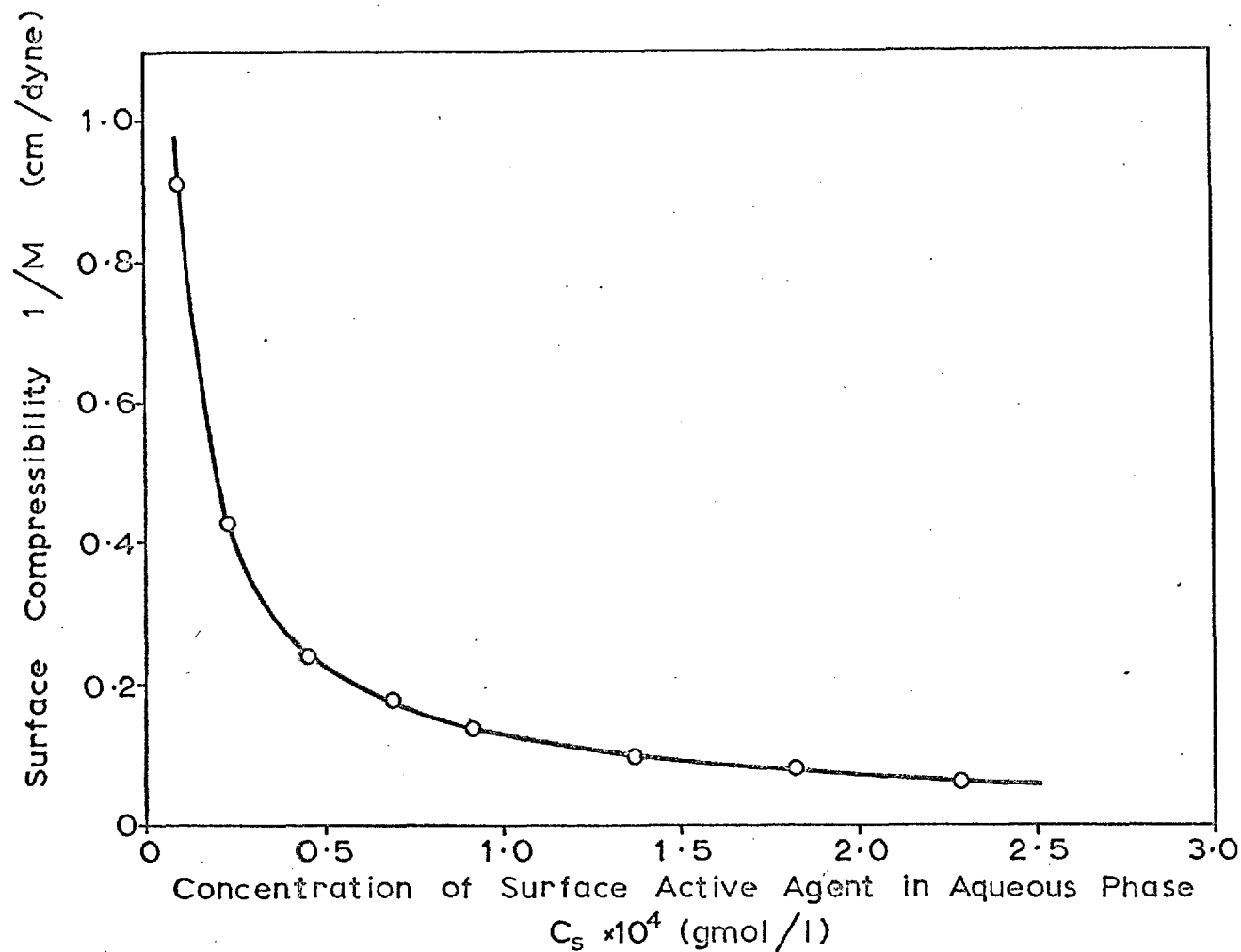


FIG. G.2 : SURFACE COMPRESSIBILITY AS A FUNCTION OF THE CONCENTRATION OF SURFACE ACTIVE AGENT TEEPOL 514 IN THE AQUEOUS PHASE

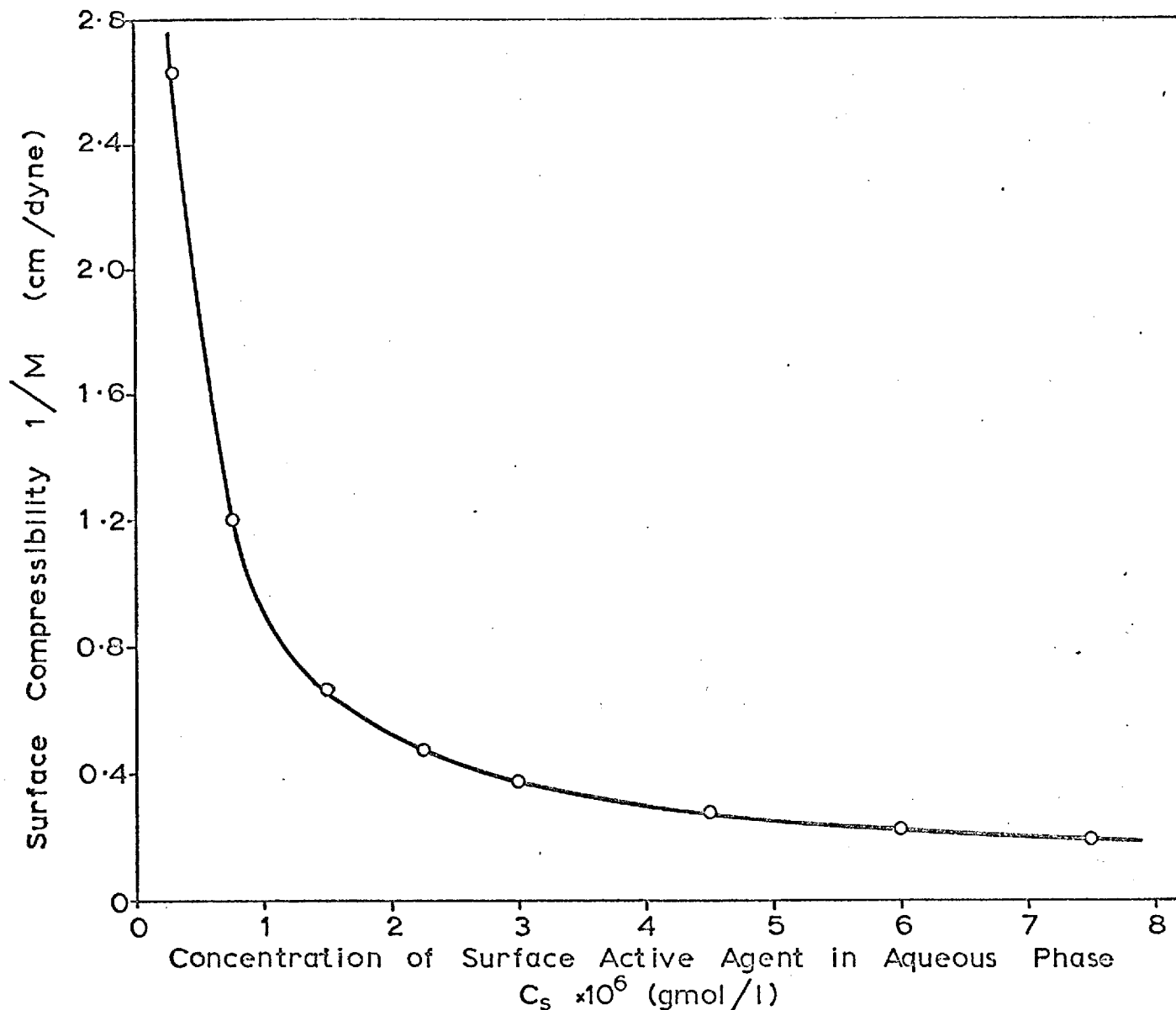


FIG. G.3 : SURFACE COMPRESSIBILITY AS A FUNCTION OF THE CONCENTRATION OF SURFACE ACTIVE AGENT MANOXOL OT IN THE AQUEOUS PHASE

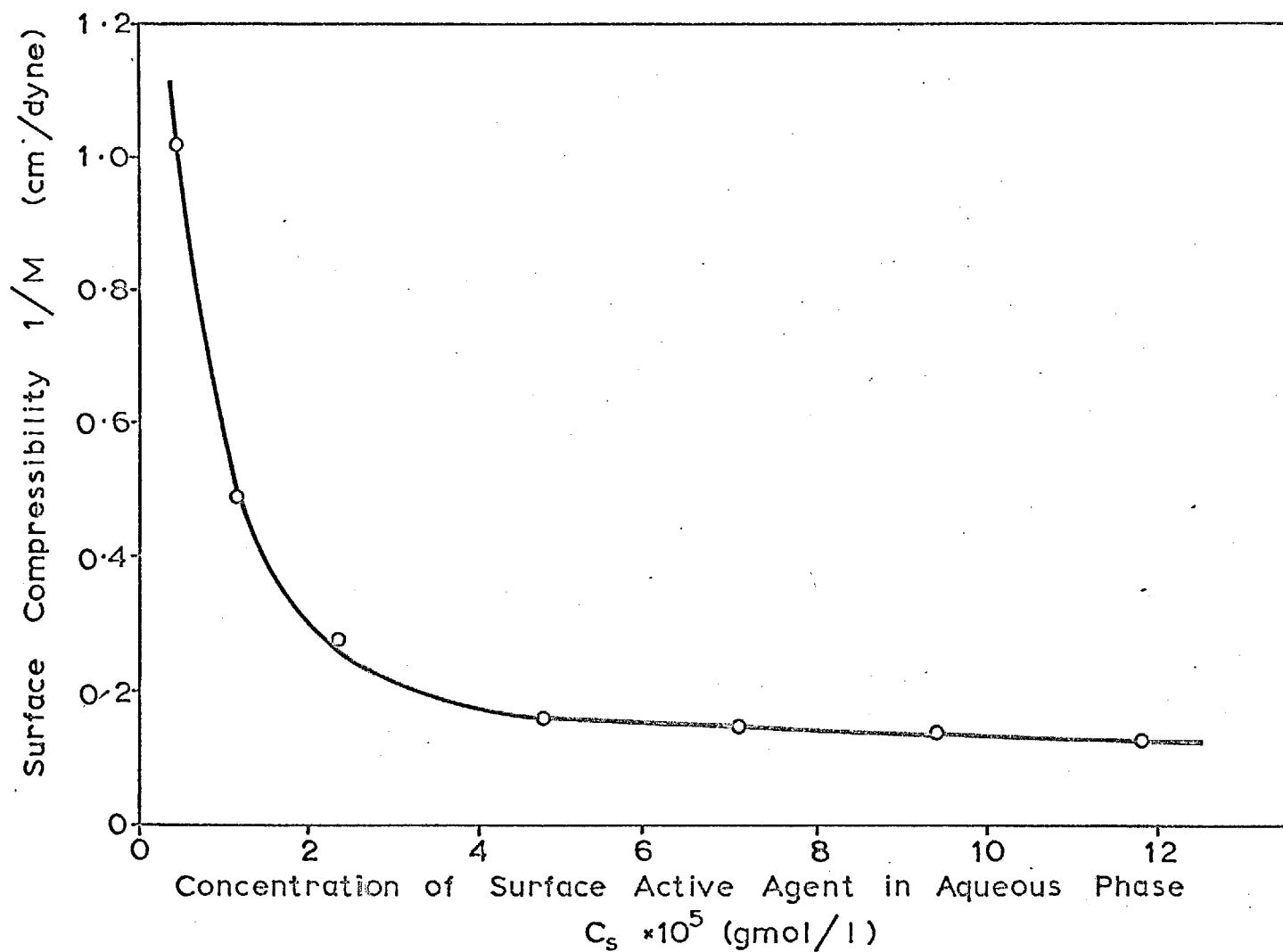


FIG. G.4 : SURFACE COMPRESSIBILITY AS A FUNCTION OF THE CONCENTRATION OF SURFACE ACTIVE AGENT LISSAPOL N IN THE AQUEOUS PHASE

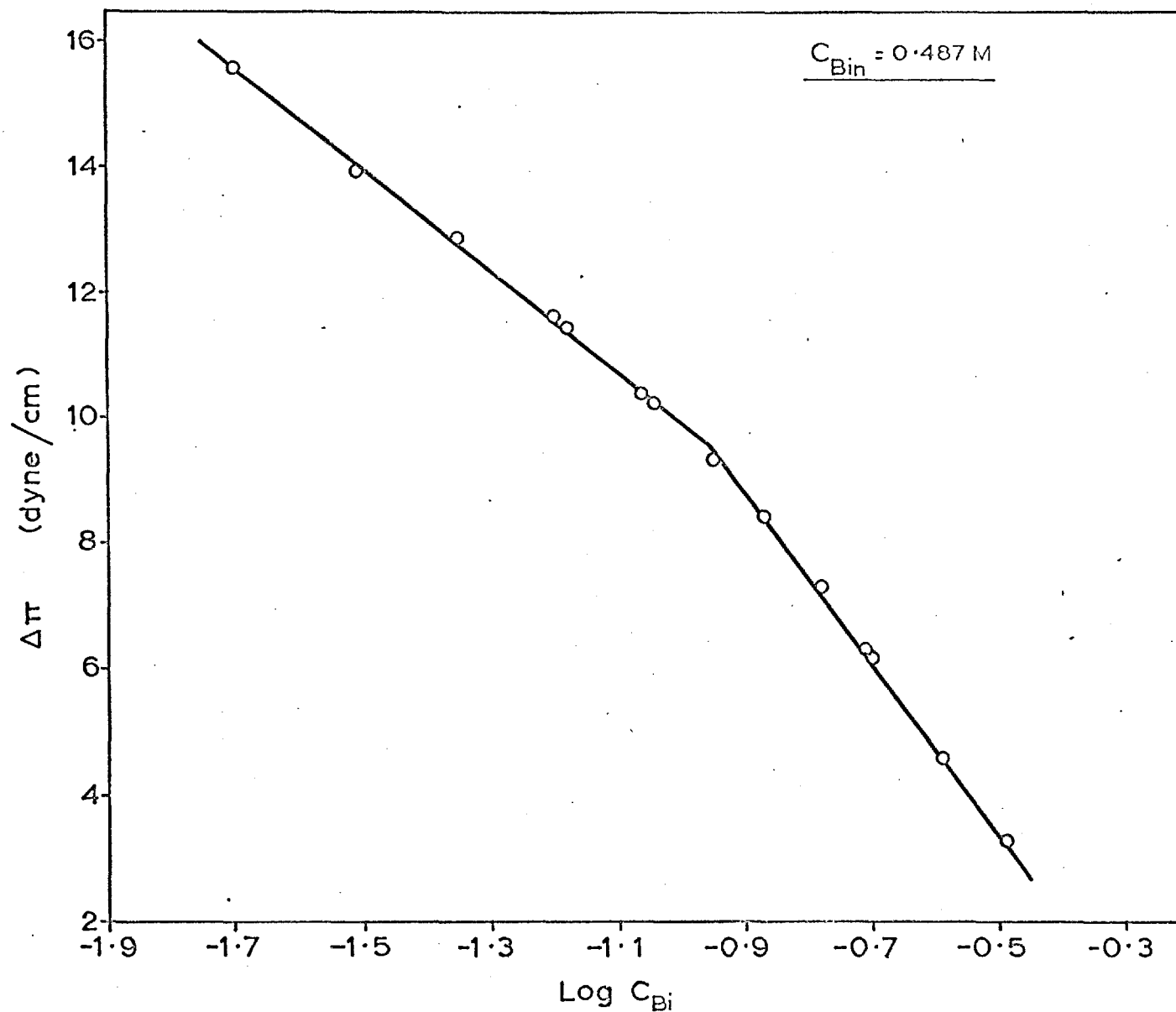


FIG. G.5: $\Delta\pi - \text{Log } C_{Bi}$ PLOT FOR THE TRANSFER OF ACETIC ACID FROM
BENZENE TO WATER

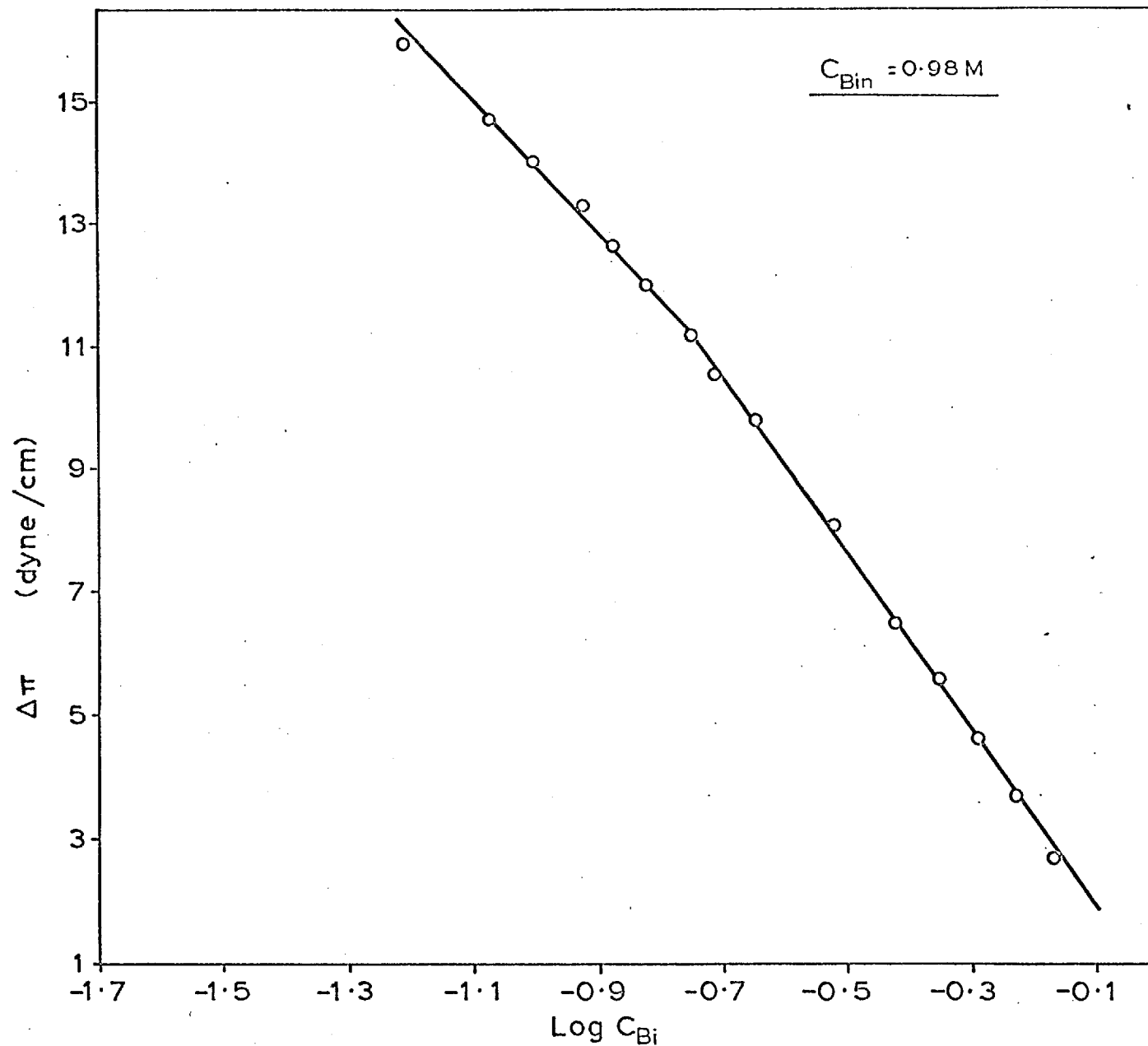


FIG. G.6 : $\Delta\pi - \text{Log } C_{Bi}$ PLOT FOR THE TRANSFER OF ACETIC ACID FROM
BENZENE TO WATER

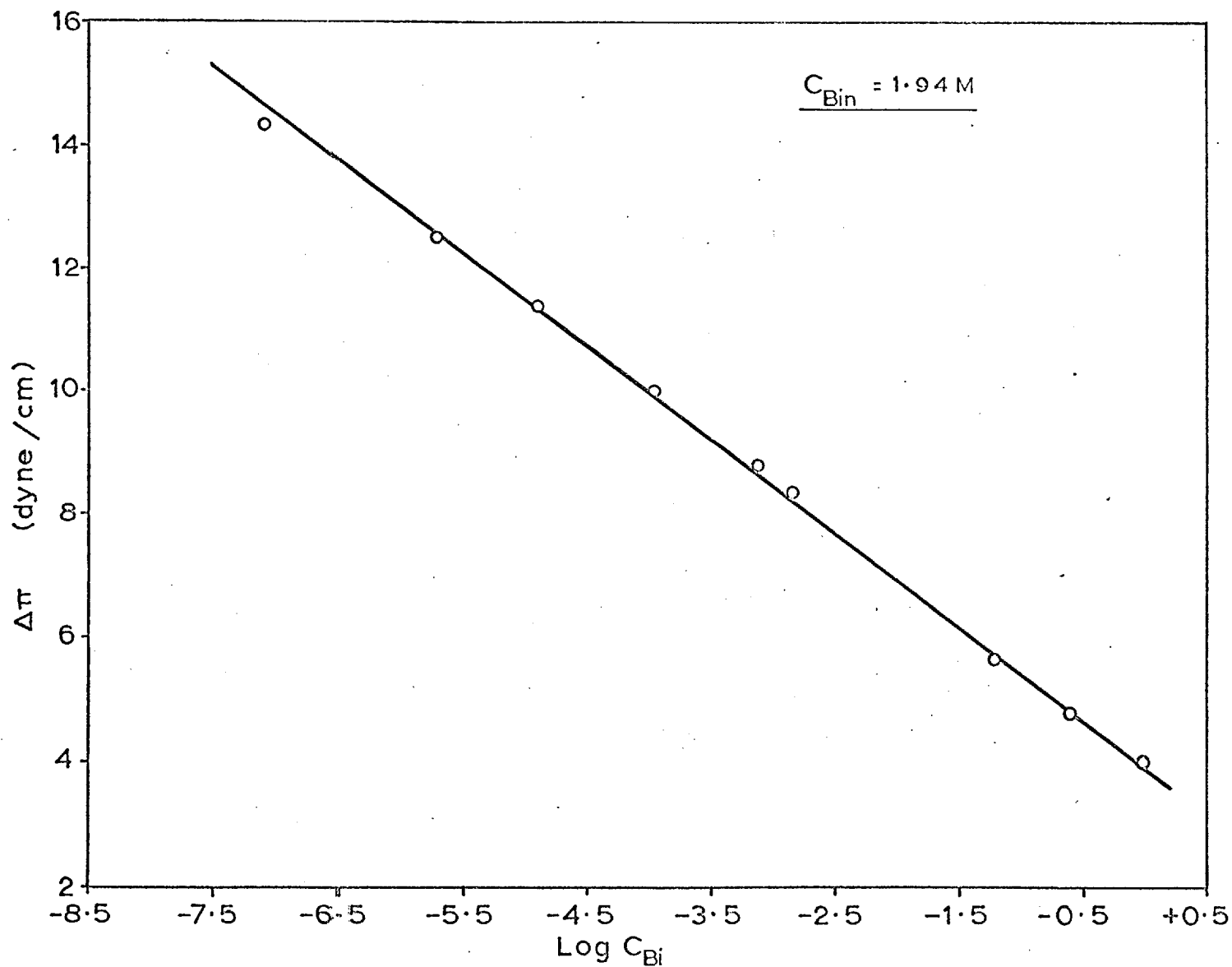


FIG. G.7: $\Delta\pi - \text{Log } C_{Bi}$ PLOT FOR THE TRANSFER OF ACETIC ACID FROM
BENZENE TO WATER

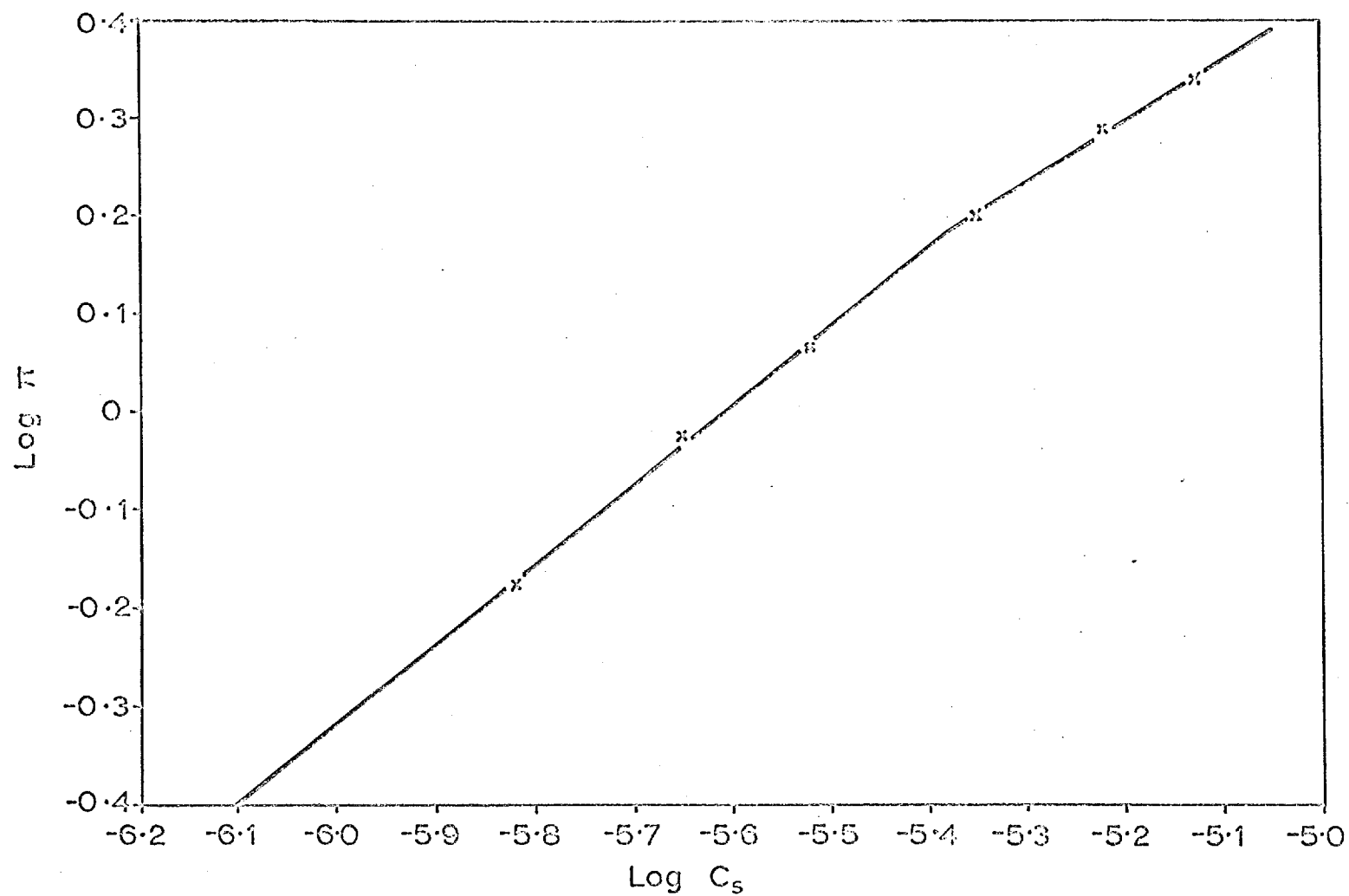


FIG. G. 8 : $\text{Log } \pi - \text{Log } C_s$ PLOT FOR SURFACE ACTIVE AGENT
DODECYLAMINE HYDROCHLORIDE

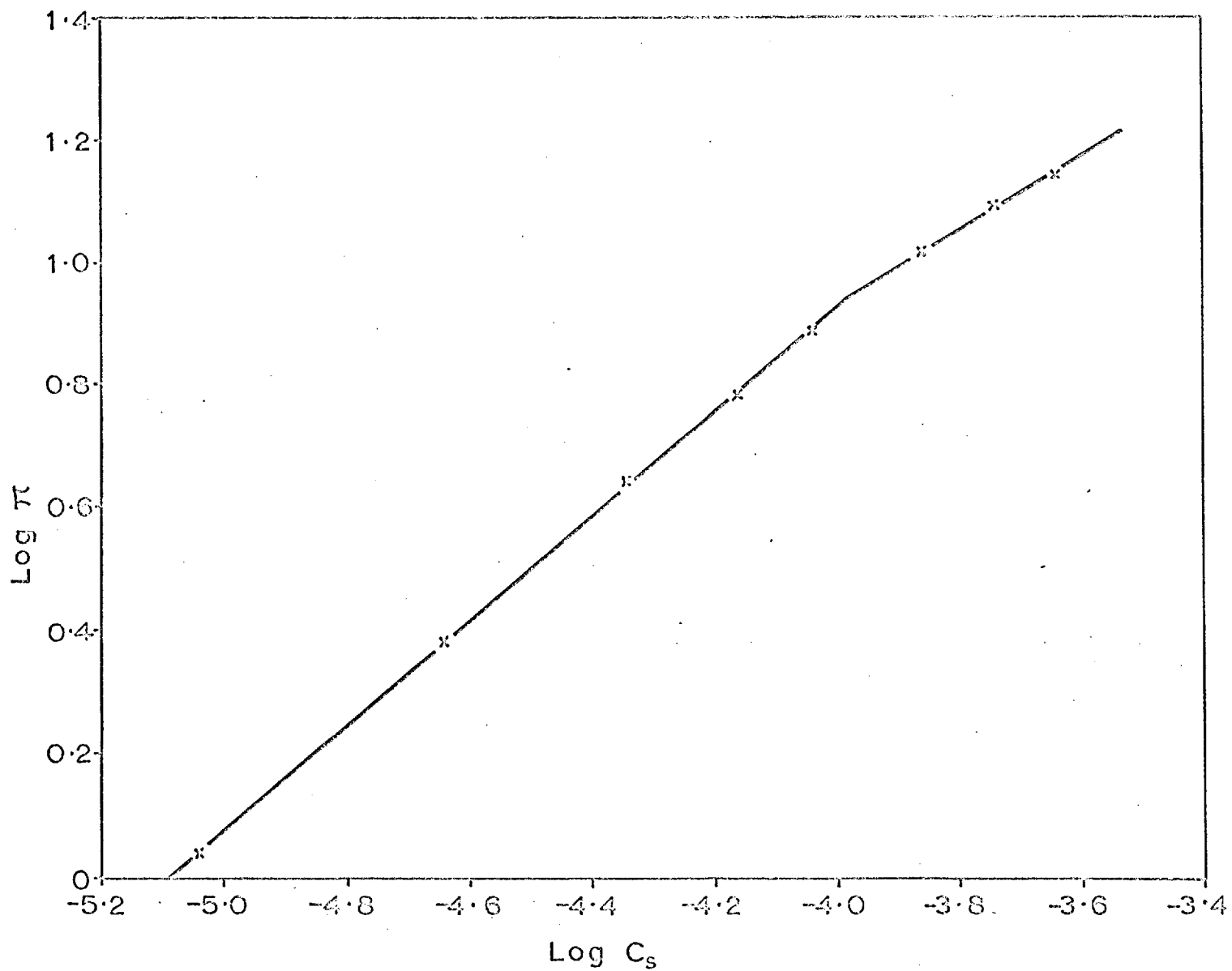


FIG. G.9 : $\text{Log } \pi$ - $\text{Log } C_s$ PLOT FOR SURFACE ACTIVE AGENT TEEPOL 514

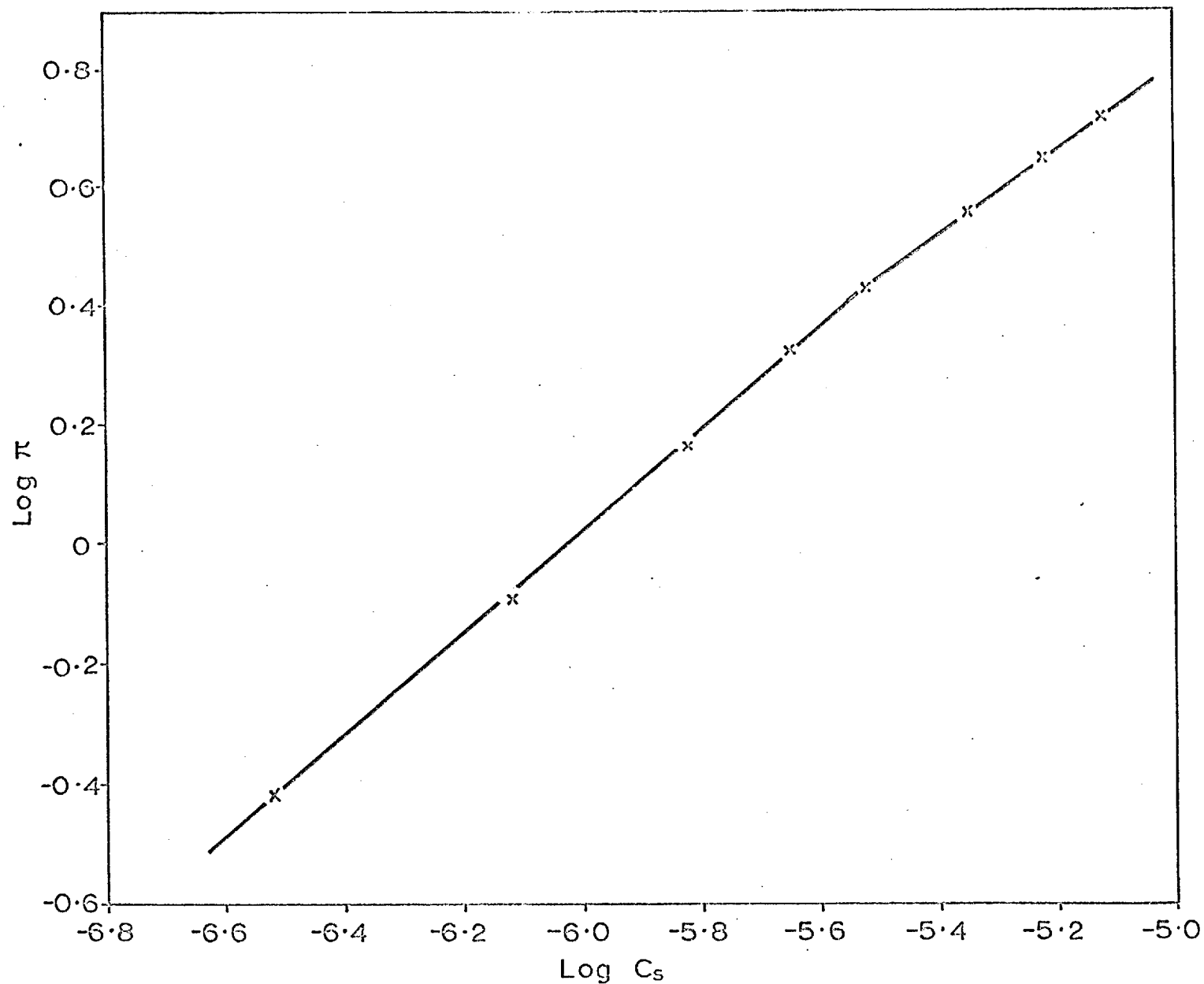


FIG. G.10 : $\text{Log } \pi - \text{Log } C_s$ PLOT FOR SURFACE ACTIVE AGENT MANOXOL OT

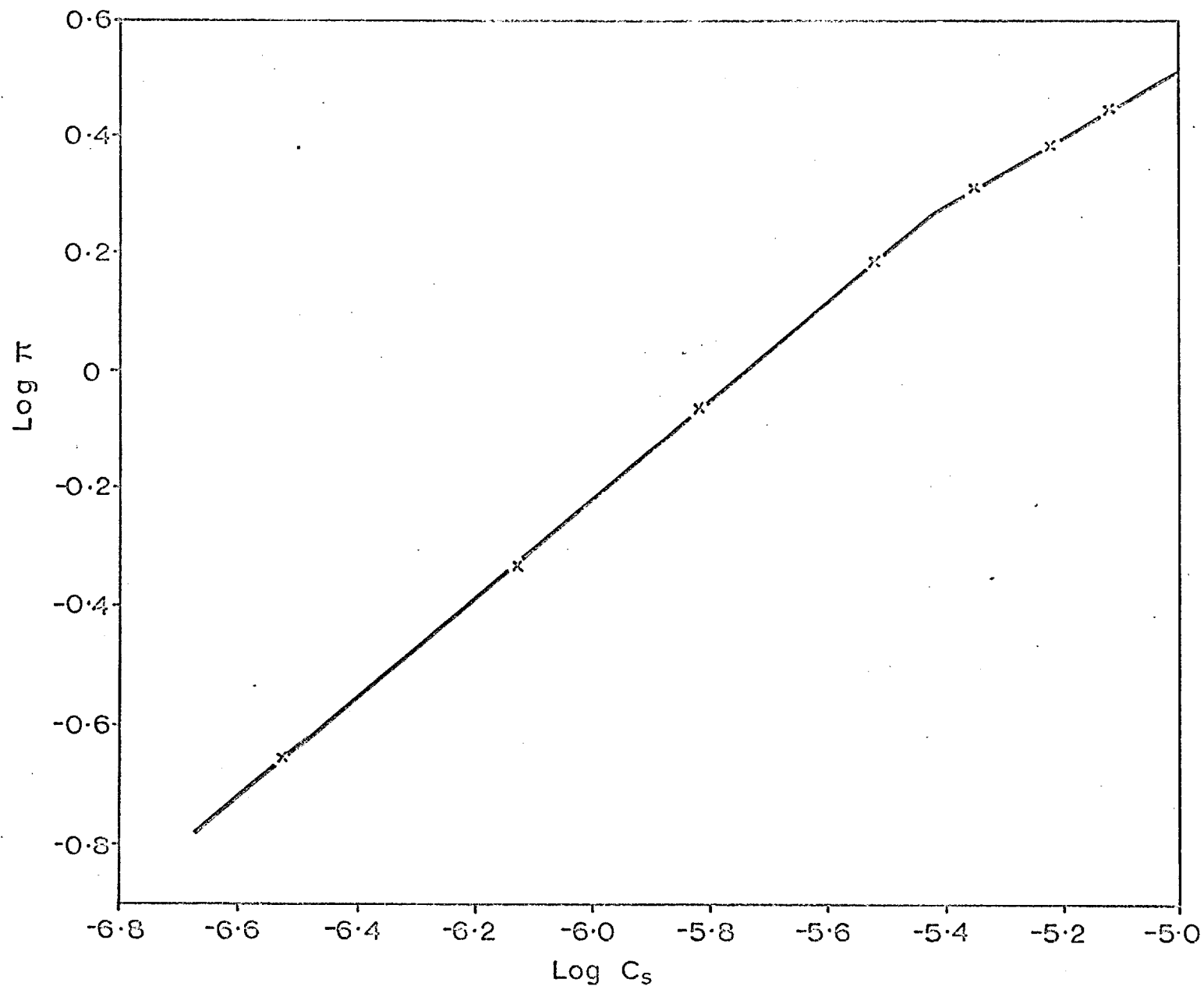


FIG. G.11 : $\text{Log } \pi$ - $\text{Log } C_s$ PLOT FOR SURFACE ACTIVE AGENT SODIUM LAURYL SULPHATE

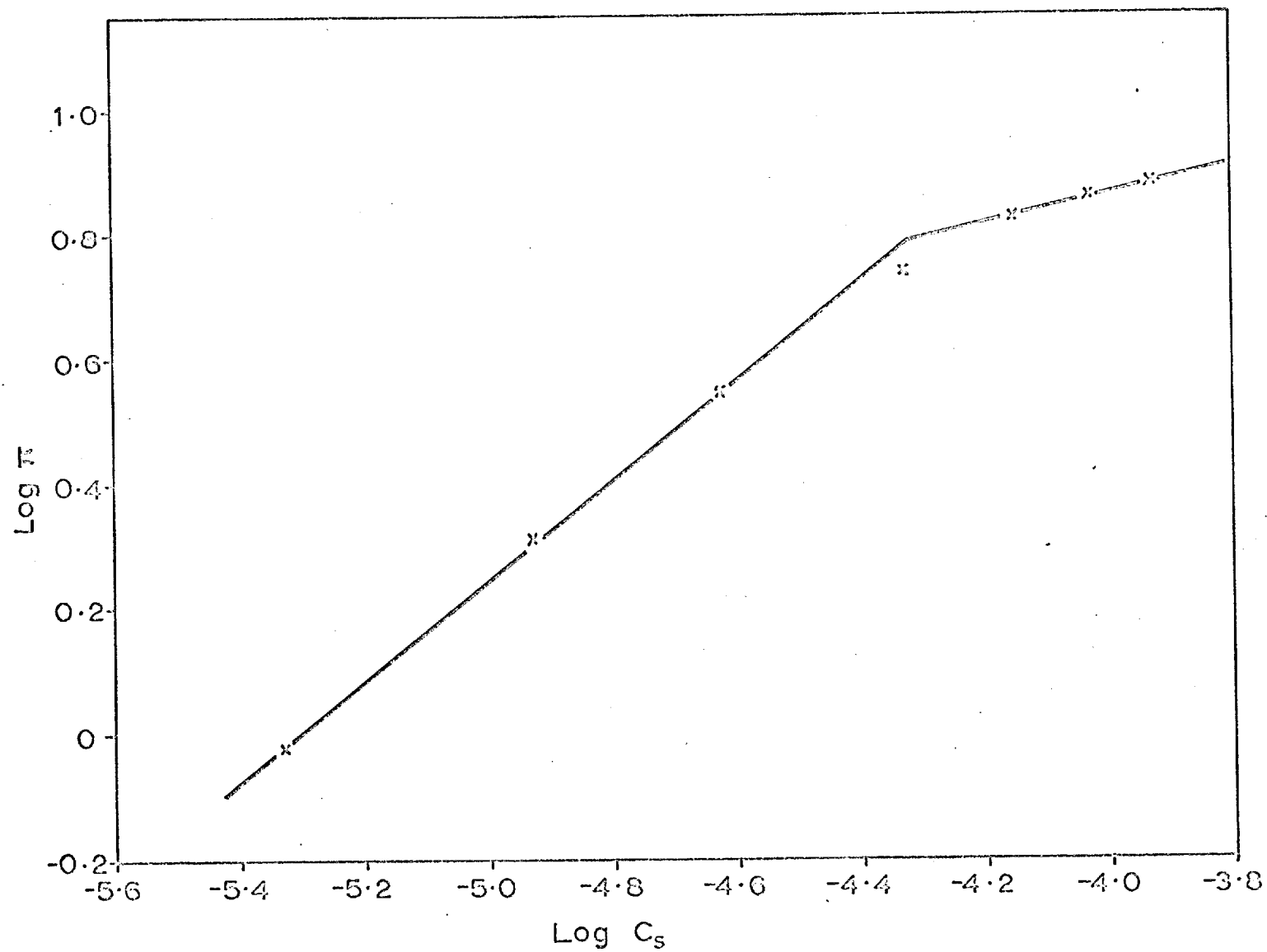


FIG. G. 12 : $\text{Log } \pi$ - $\text{Log } C_s$ PLOT FOR SURFACE ACTIVE AGENT LISSAPOL N

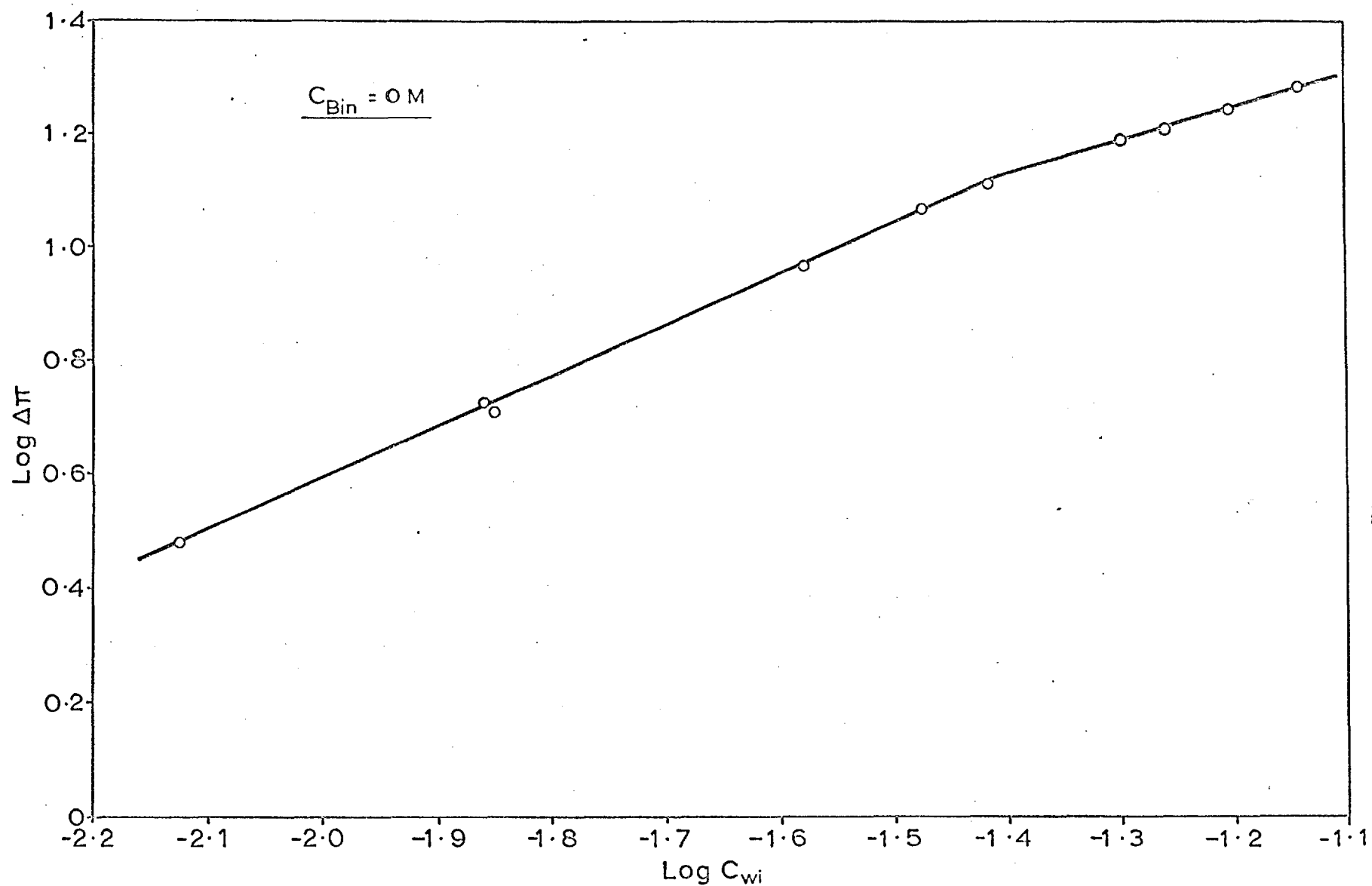


FIG. G.13 : $\text{Log } \Delta\pi - \text{Log } C_{wi}$ PLOT FOR THE TRANSFER OF PHENOL FROM WATER TO BENZENE

APPENDIX H

Interfacial Properties

Table I - Absence of Surface Active Agents

Runs 1 - 16 ... Transfer of Acetic Acid from Benzene Drop to Water
 $C_{B \text{ in}}$ constant at 0.487 M

Run	C_{wi}	C_{Bi}	$\Delta\pi$	$1/M_i$	$\Delta\pi/M_i$	$\frac{1}{\eta_{si}} \cdot 10^{-4}$	$\Delta\pi/\eta_{si}$	$K_{od} \cdot 10^2$
1	.69	.02	15.6	.187	2.92	1.28	20.0	.994
2	.96	.031	13.9	.159	2.21	1.22	17.0	.816
3	1.17	.045	12.9	.146	1.88	1.18	15.2	.658
4	1.42	.063	11.6	.138	1.60	1.16	13.5	.421
5	1.46	.066	11.4	.138	1.57	1.16	13.2	.426
6	1.71	.088	10.3	.115	1.18	1.12	11.5	.414
7	1.72	.091	10.2	.115	1.17	1.12	11.4	.409
8	1.93	.111	9.3	.082	.76	1.10	10.2	.556
9	2.15	.134	8.4	.081	.68	1.09	9.2	.475
10	2.16	.135	8.4	.080	.67	1.09	9.2	.403
11	2.46	.167	7.3	.079	.58	1.07	7.8	.380
12	2.72	.194	6.3	.078	.49	1.06	6.7	.421
13	2.76	.198	6.2	.078	.48	1.06	6.6	.441
14	3.22	.260	4.6	.077	.35	1.03	4.7	.431
15	3.22	.260	4.6	.077	.35	1.03	4.7	.386
16	3.69	.325	3.3	.076	.25	1.02	3.5	.414

Runs 17 - 31 ... Transfer of Acetic Acid from Benzene Drop to Water
 $C_{B \text{ in}}$ constant at 0.98 M

17	1.43	.062	15.9	.106	1.69	1.14	18.1	1.710
18	1.67	.085	14.7	.089	1.31	1.12	16.5	1.43
19	1.85	.100	14.0	.087	1.22	1.11	15.5	1.30
20	2.01	.120	13.3	.086	1.14	1.10	14.6	1.18
21	2.17	.136	12.7	.085	1.08	1.09	13.8	1.10
22	2.35	.153	12.0	.085	1.02	1.08	13.0	.95
23	2.57	.179	11.2	.084	.94	1.06	11.9	.88
24	2.74	.195	10.5	.086	.90	1.05	11.0	.83
25	2.96	.223	9.8	.085	.83	1.04	10.2	.75
26	3.51	.300	8.1	.084	.68	1.02	8.3	.66
27	4.05	.379	6.5	.083	.54	1.01	6.6	.56
28	4.50	.488	5.6	.083	.46	1.00	5.6	.416
29	4.94	.518	4.6	.082	.38	1.00	4.6	.387
30	5.35	.589	3.7	.082	.30	.99	3.7	.390
31	5.85	.681	2.7	.082	.22	.99	2.7	.402

Runs 32 - 40 ... Transfer of Acetic Acid from Benzene Drop to Water
(for column heads see previous page) C_B in constant at 1.94 M

32	2.76	.196	14.3	.070	1.00	1.05	15.0	2.00
33	3.28	.269	12.5	.069	.86	1.03	12.9	1.72
34	3.69	.375	11.4	.068	.77	1.02	11.6	1.45
35	4.23	.403	10.0	.068	.68	1.00	10.0	1.25
36	4.76	.489	8.8	.067	.59	.99	8.8	.951
37	4.94	.519	8.4	.067	.56	.98	8.2	.802
38	6.21	.753	5.7	.067	.38	.95	5.4	.584
39	6.71	.871	4.8	.067	.32	.94	4.5	.399
40	7.20	.997	4.0	.067	.27	.94	3.8	.419

Runs 144 - 153 ... Transfer of Phenol from Water to a Benzene Drop
 C_B in constant at 0.0 M

144	.0075		3.0	.33	.99	.85	2.55	.142
145	.0141		5.1	.187	.95	.67	3.42	.120
146	.0147		5.4	.192	1.04	.67	3.62	.133
147	.0263		9.3	.107	.99	.645	6.0	.143
148	.0335		11.6	.078	.90	.645	7.5	.149
149	.0384		12.9	.077	.99	.645	8.3	.176
150	.0505		15.5	.076	1.18	.640	9.9	.248
151	.0550		16.2	.076	1.23	.640	10.4	.325
152	.0629		17.5	.075	1.31	.637	11.1	.455
153	.0725		19.4	.075	1.45	.637	12.4	.629

Table II - Presence of Surface Active Agents

Of each of the five surface active agents tabulated below, in each case the transfer was of acetic acid from a benzene drop to water.

Runs 44 - 51 ... Surface active agent - Dodecylamine Hydrochloride

Run	$C_s \cdot 10^6$	π	$1/M$	$(1/\eta_s)10^{-4}$	$K_{od} \cdot 10^2$
44	0.0	0.0	∞		1.775
45	.75	.38	2.64	7.7	.959
46	1.5	.67	1.52	3.7	.679
47	2.25	.94	1.08	2.4	.383
48	3.0	1.16	.91	1.41	.419
49	4.5	1.58	.64	.78	.419
50	6.0	1.94	.55	.75	.405
51	7.5	2.19	.48	.72	.415

Runs 68 - 76 ... Surface active agent - Teepol 514

68	0.0	0.0	∞		1.790
69	9.1	1.1	.91	3.7	.585
70	22.8	2.4	.43	1.54	.354
71	45.6	4.4	.24	.62	.390
72	68.5	6.1	.178	.40	.406
73	91.3	7.7	.135	.37	.400
74	136.9	10.3	.100	.34	.380
75	182.5	12.4	.083	.33	.440
76	228.2	13.8	.063	.32	.408

Runs 104 - 112 ... Surface active agent - Manoxol OT

104	0.0	0.0	∞		1.830
105	0.3	0.38	2.64	4.8	1.001
106	.75	.8	1.21	1.96	.770
107	1.5	1.46	.67	.98	.546
108	2.25	2.09	.48	.66	.436
109	3.00	2.65	.38	.60	.385
110	4.50	3.6	.28	.56	.309
111	6.0	4.46	.23	.53	.335
112	7.5	5.2	.20	.51	.324

Runs 113 - 121 ... Surface active agent - Sodium Lauryl Sulphate

Run	$C_s \cdot 10^6$	π	$1/M$	$(1/\eta_s) 10^{-4}$	$K_{od} \cdot 10^2$
113	0.0	0.0	∞		1.780
114	.3	.22	4.55	11.1	.657
115	.75	.46	2.08	4.16	.467
116	1.5	.86	1.18	1.89	.491
118	3.0	1.52	.57	.62	.449
119	4.5	2.04	.50	.60	.399
120	6.0	2.43	.44	.59	.412
121	7.5	2.8	.38	.59	.369

Runs 122 - 130 ... Surface active agent - Lissapol N

122	0.0	0.0	∞		1.736
123	4.7	.95	1.02	1.18	.505
124	11.8	2.0	.49	.67	.419
125	23.5	3.5	.28	.51	.398
127	47.1	5.45	.20	.49	.315
128	70.6	6.6	.15	.49	.380
129	94.2	7.2	.14	.48	.420
130	117.9	7.6	.13	.48	.390

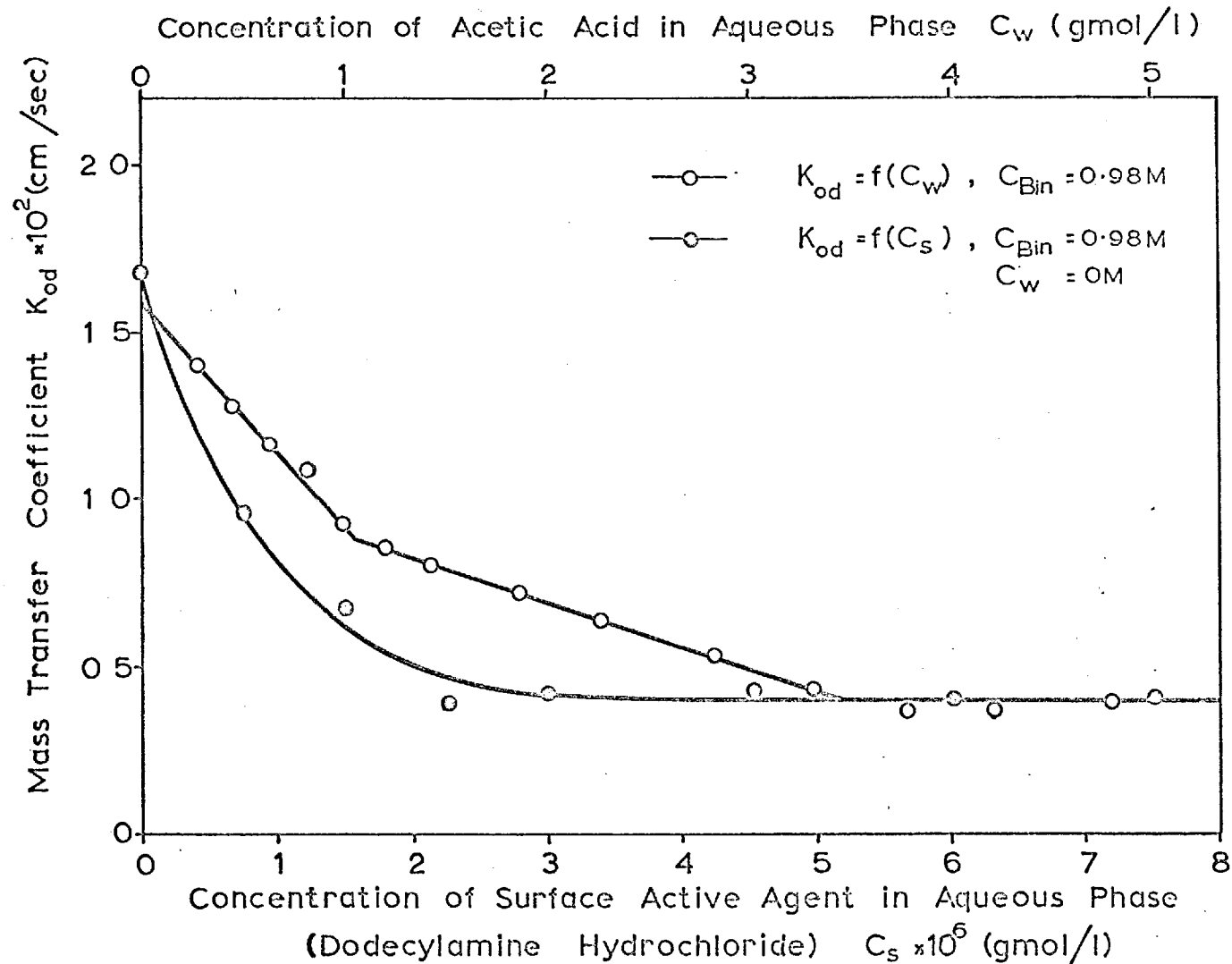


FIG. H.1: EFFECT OF SURFACE ACTIVE AGENT ON THE MASS TRANSFER RATE

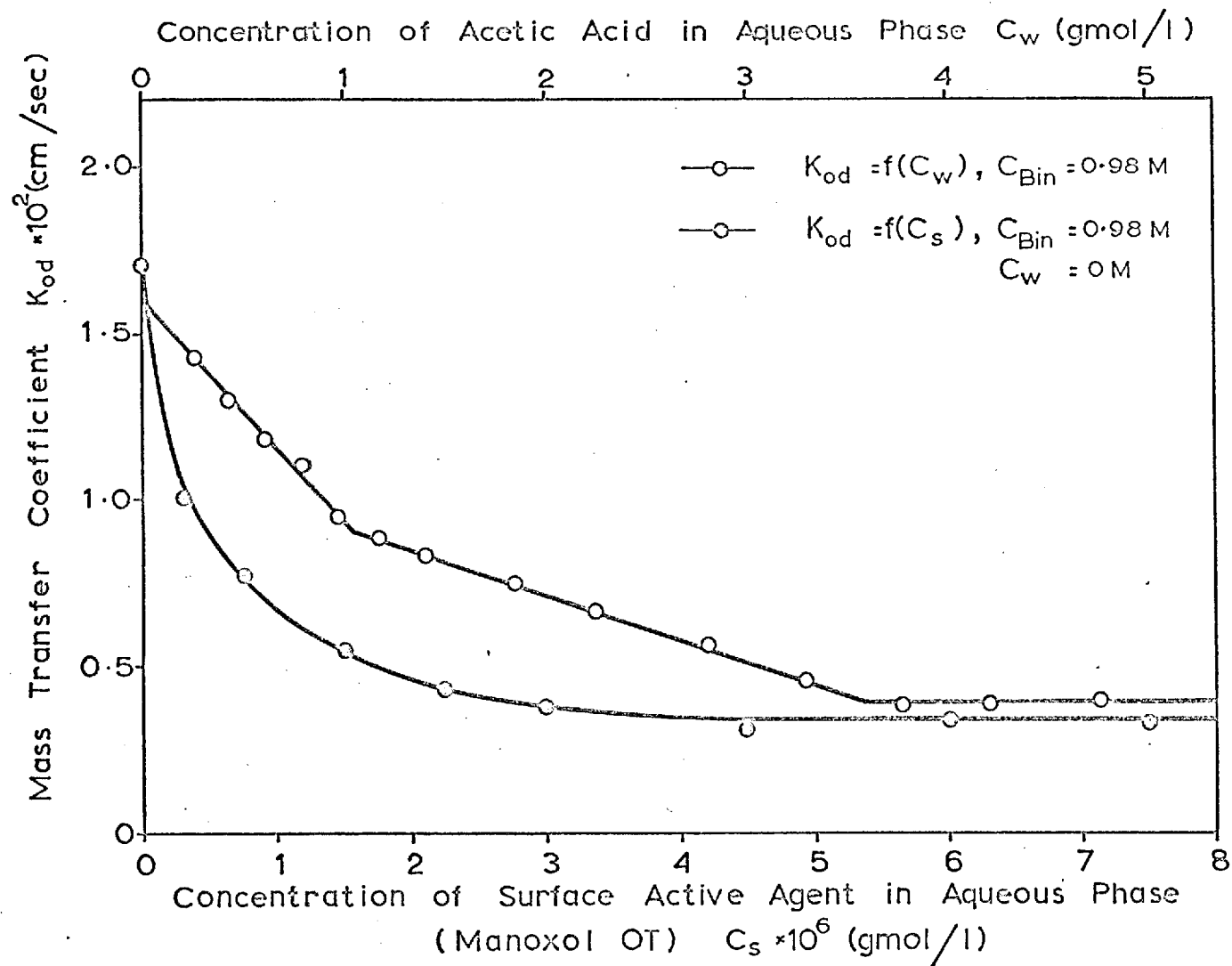


FIG. H.2 : EFFECT OF SURFACE ACTIVE AGENT ON THE MASS TRANSFER RATE

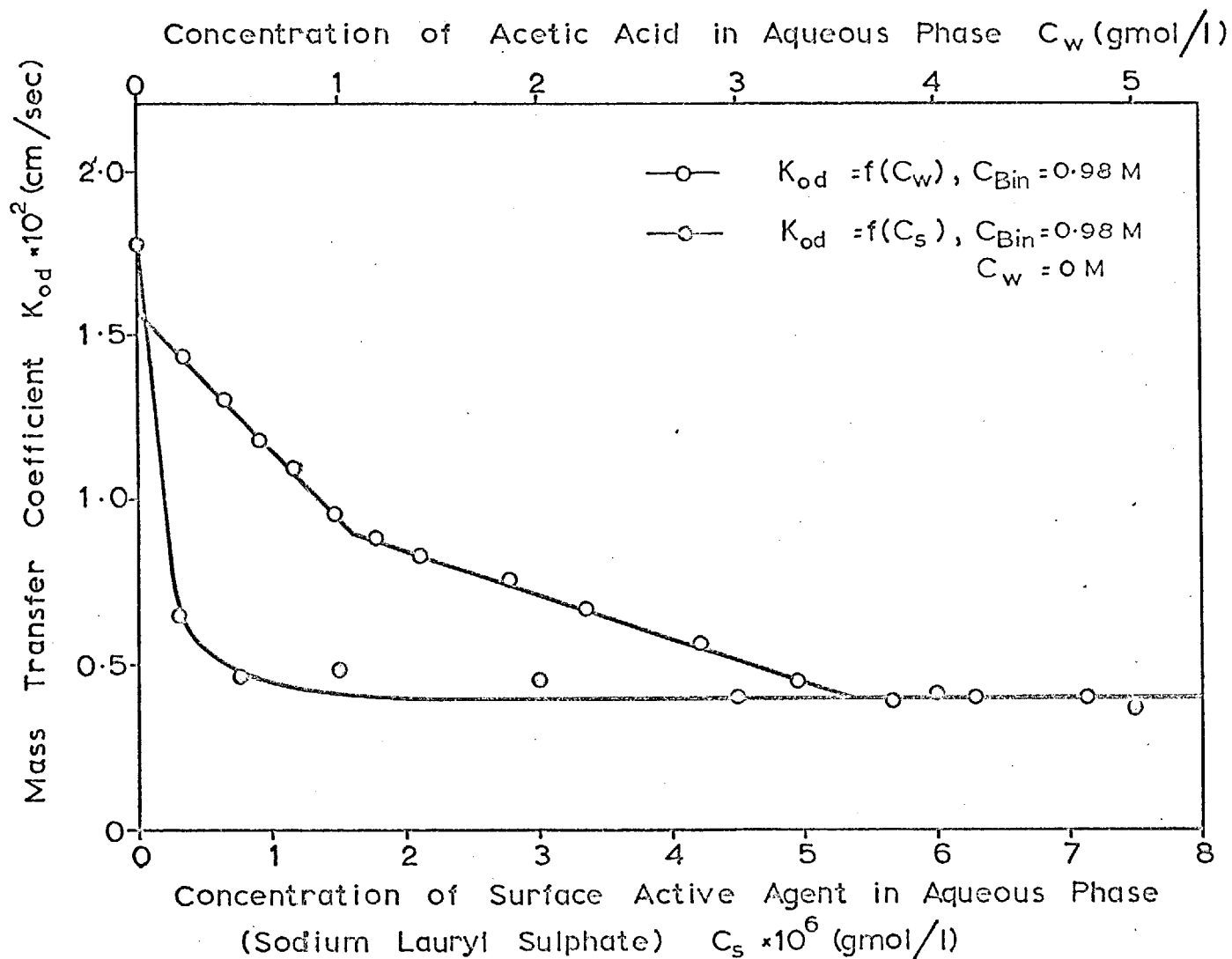


FIG. H.3 : EFFECT OF SURFACE ACTIVE AGENT ON THE MASS TRANSFER RATE

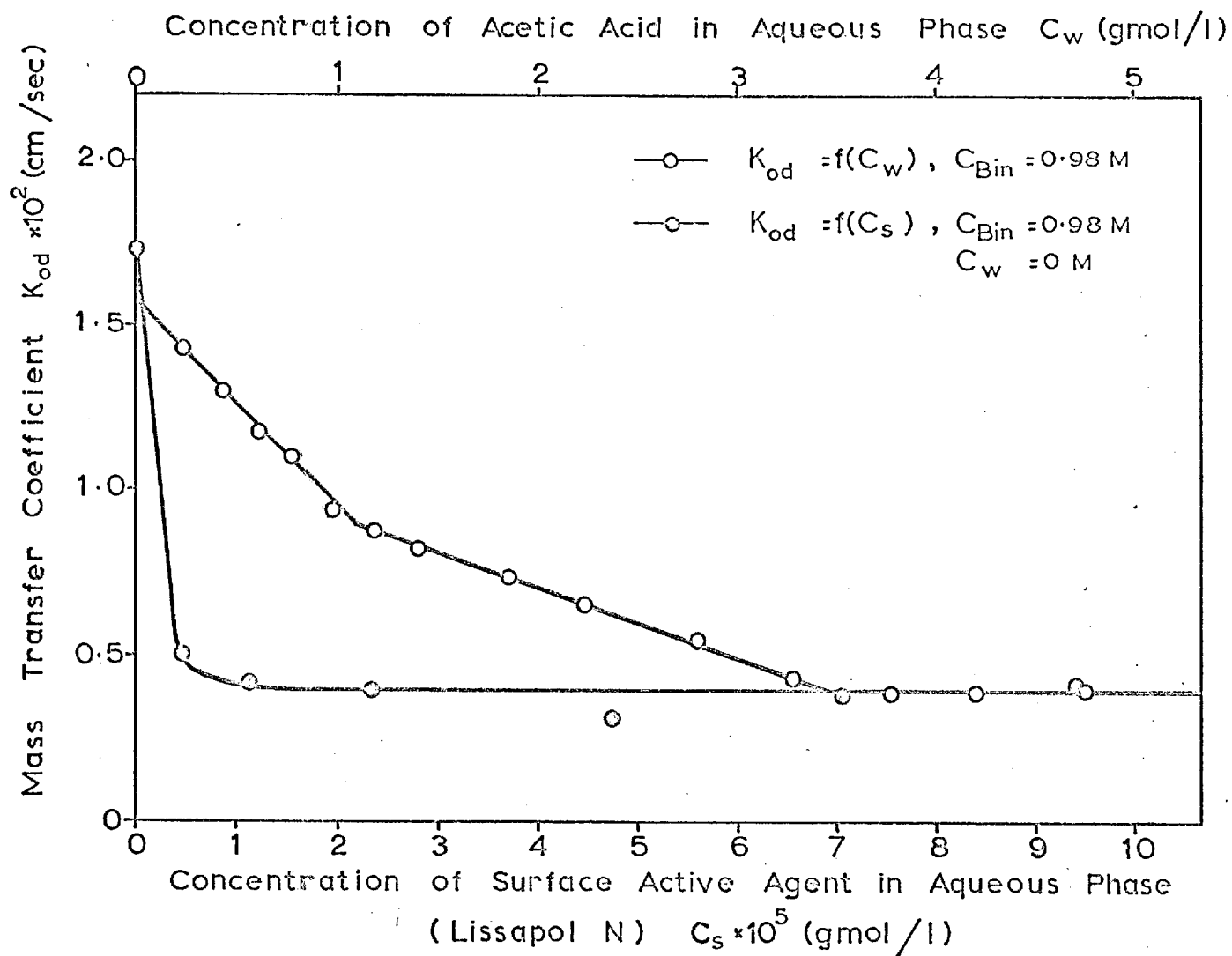


FIG. H.4 : EFFECT OF SURFACE ACTIVE AGENT ON THE MASS TRANSFER RATE

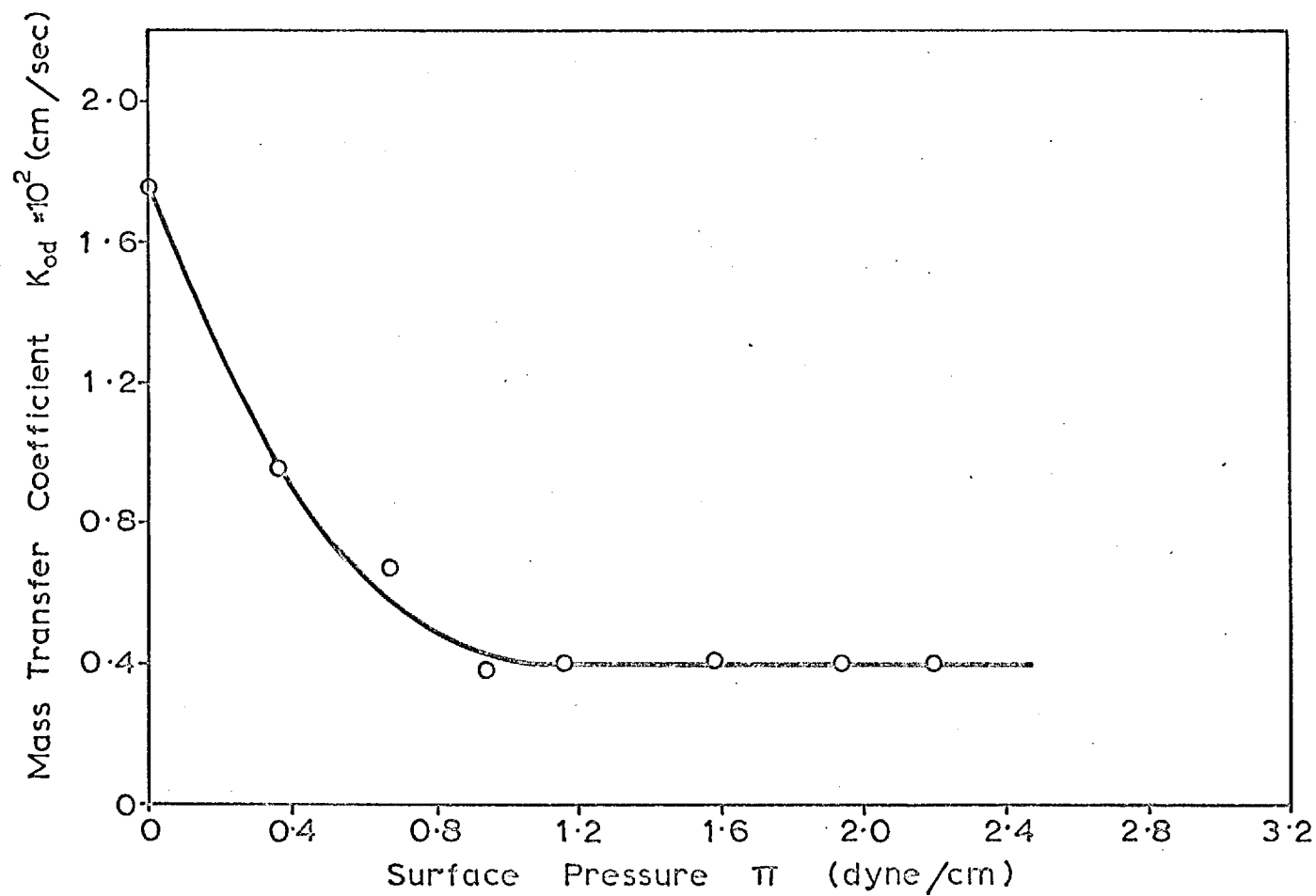


FIG. H.5: MASS TRANSFER COEFFICIENT AS A FUNCTION OF SURFACE PRESSURE
FOR SURFACE ACTIVE AGENT DODECYLAMINE HYDROCHLORIDE

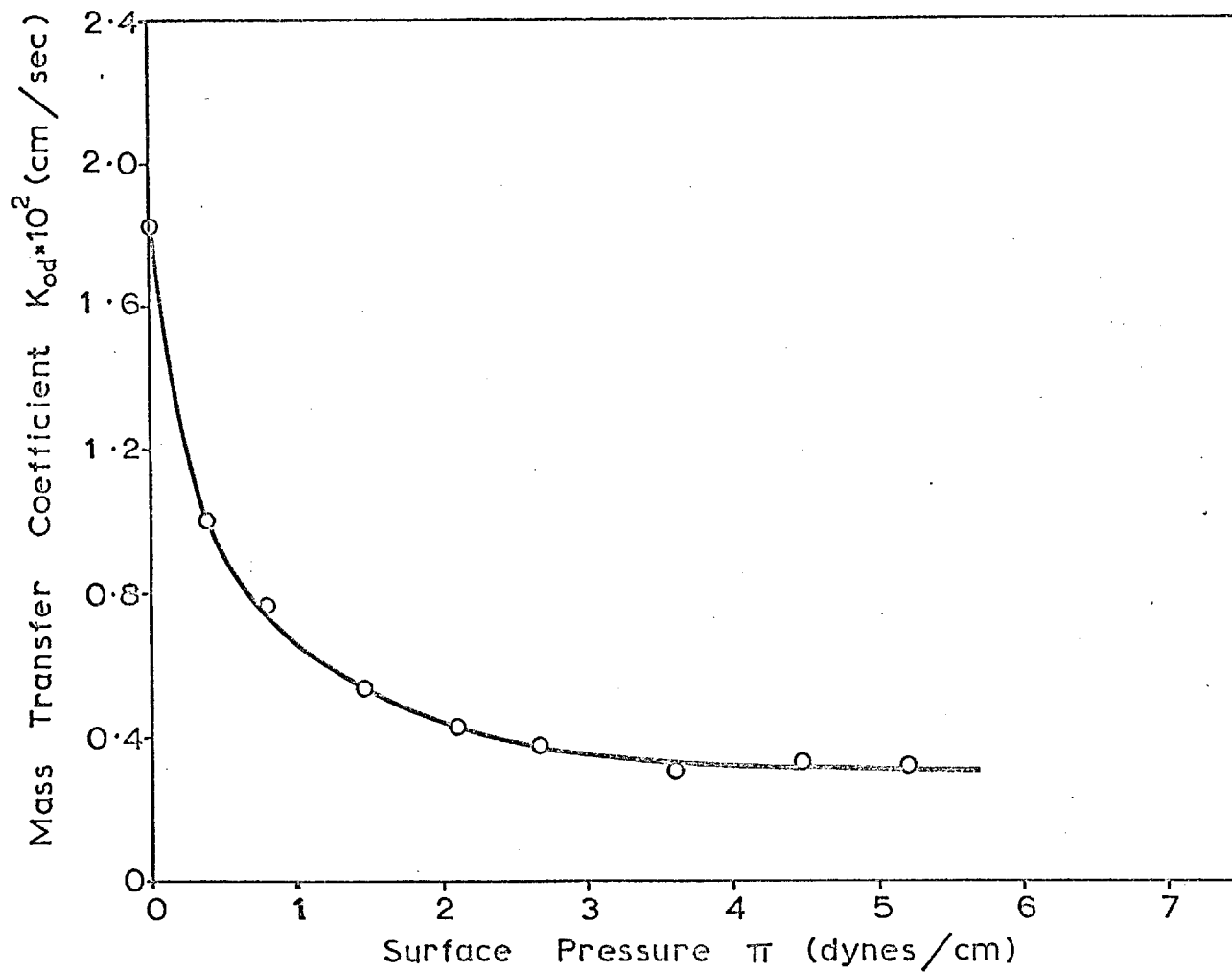


FIG. H.6 : MASS TRANSFER COEFFICIENT AS A FUNCTION OF SURFACE PRESSURE FOR SURFACE ACTIVE AGENT MANOXOL OT

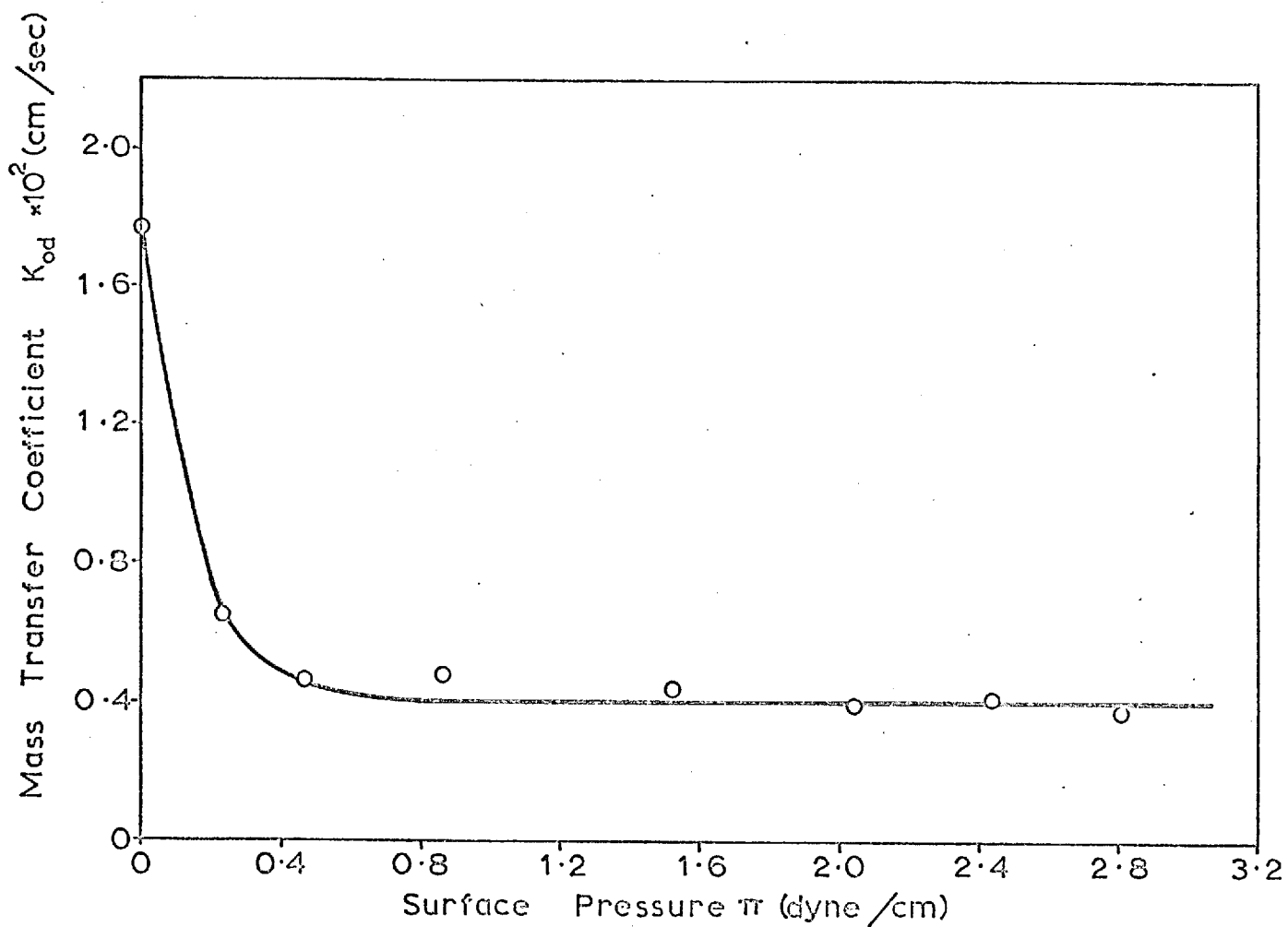


FIG. H.7: MASS TRANSFER COEFFICIENT AS A FUNCTION OF SURFACE PRESSURE
FOR SURFACE ACTIVE AGENT SODIUM LAURYL SULPHATE

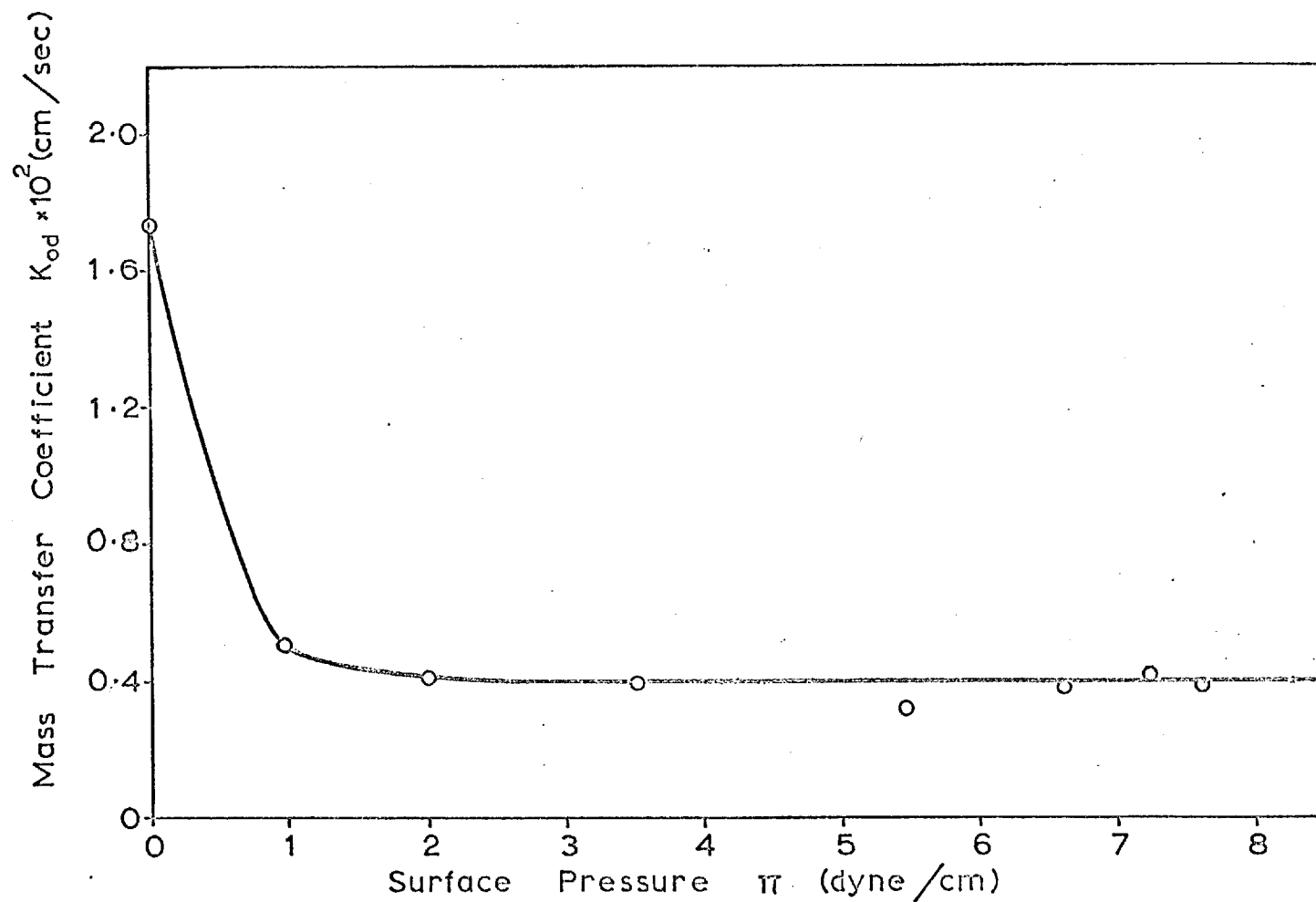


FIG. H.8 : MASS TRANSFER COEFFICIENT AS A FUNCTION OF SURFACE PRESSURE FOR SURFACE ACTIVE AGENT LISSAPOL N

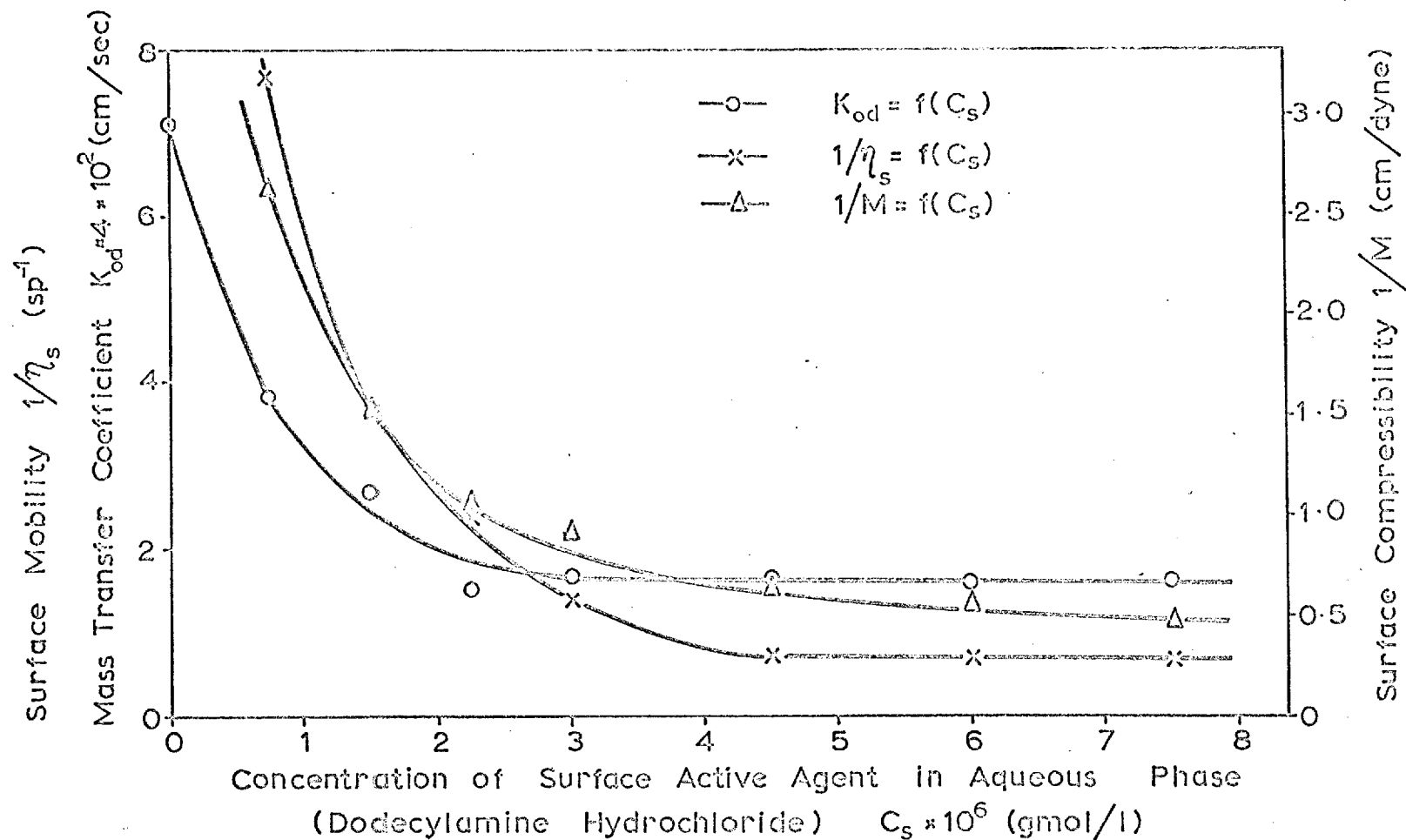


FIG. H.9. MASS TRANSFER COEFFICIENT, SURFACE MOBILITY AND SURFACE COMPRESSIBILITY AS A FUNCTION OF SURFACE ACTIVE AGENT CONCENTRATION

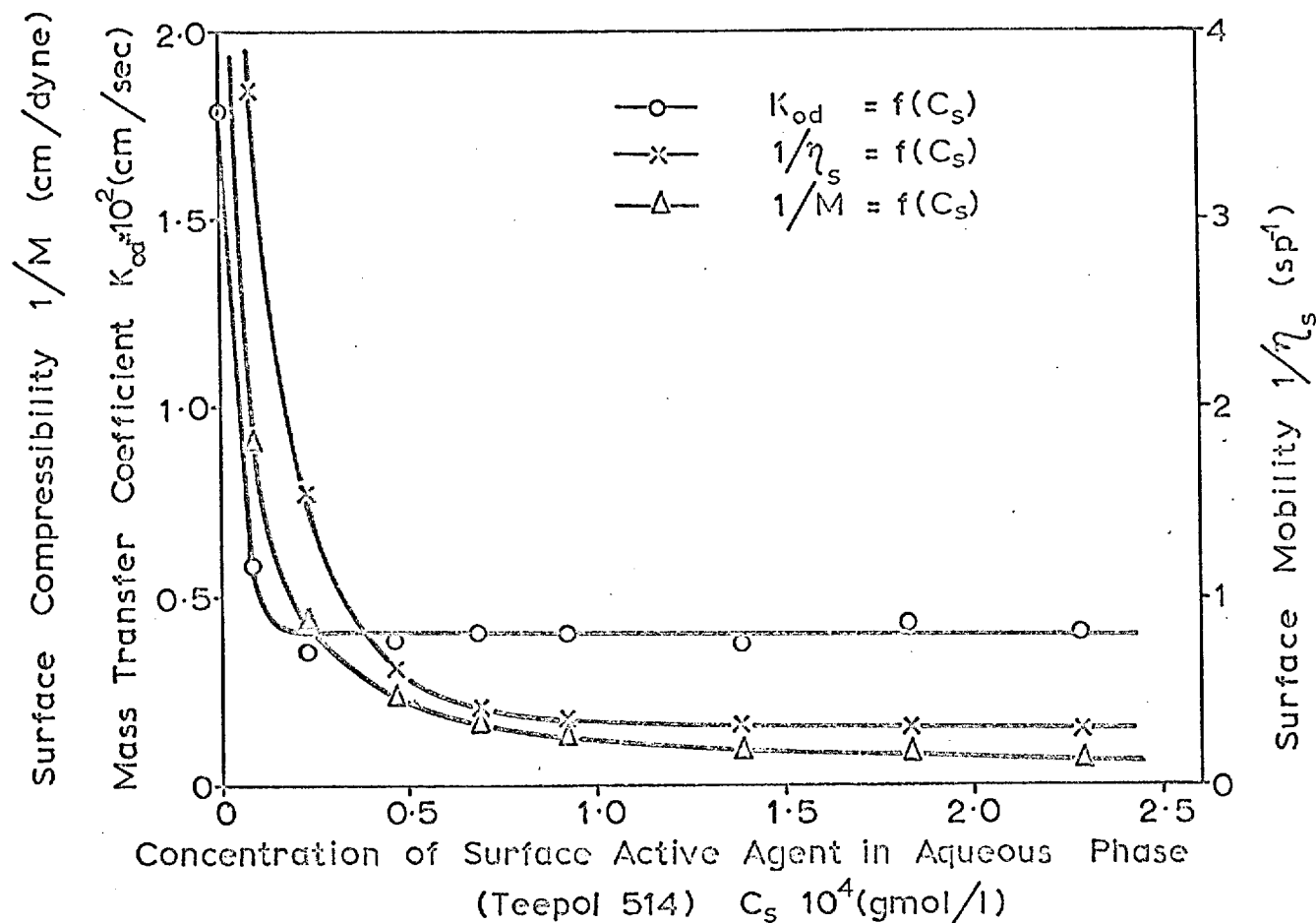


FIG. H.10: MASS TRANSFER COEFFICIENT, SURFACE MOBILITY AND SURFACE COMPRESSIBILITY AS A FUNCTION OF SURFACE ACTIVE AGENT CONCENTRATION

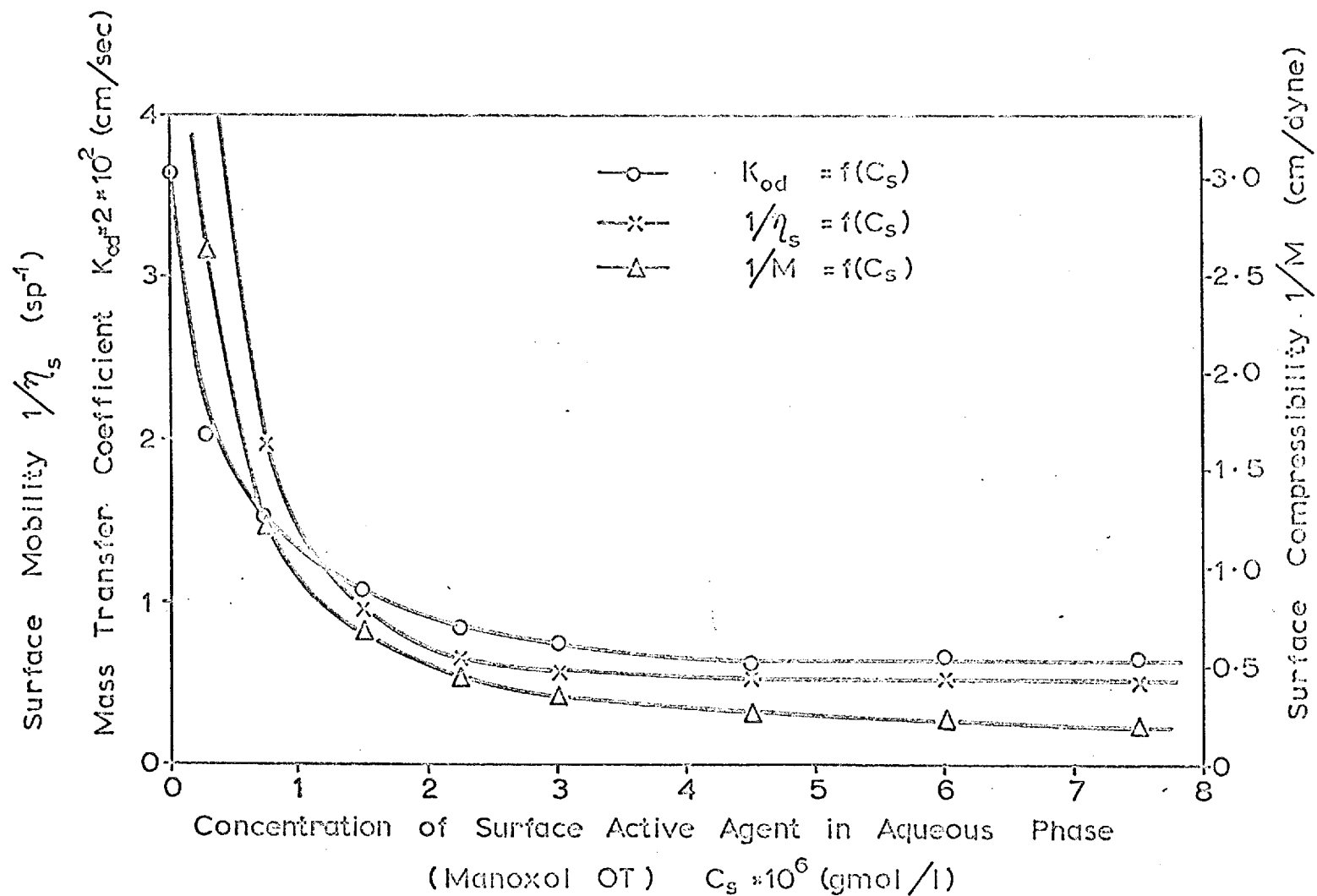


FIG. H.11: MASS TRANSFER COEFFICIENT, SURFACE MOBILITY AND SURFACE COMPRESSIBILITY AS A FUNCTION OF SURFACE ACTIVE AGENT CONCENTRATION

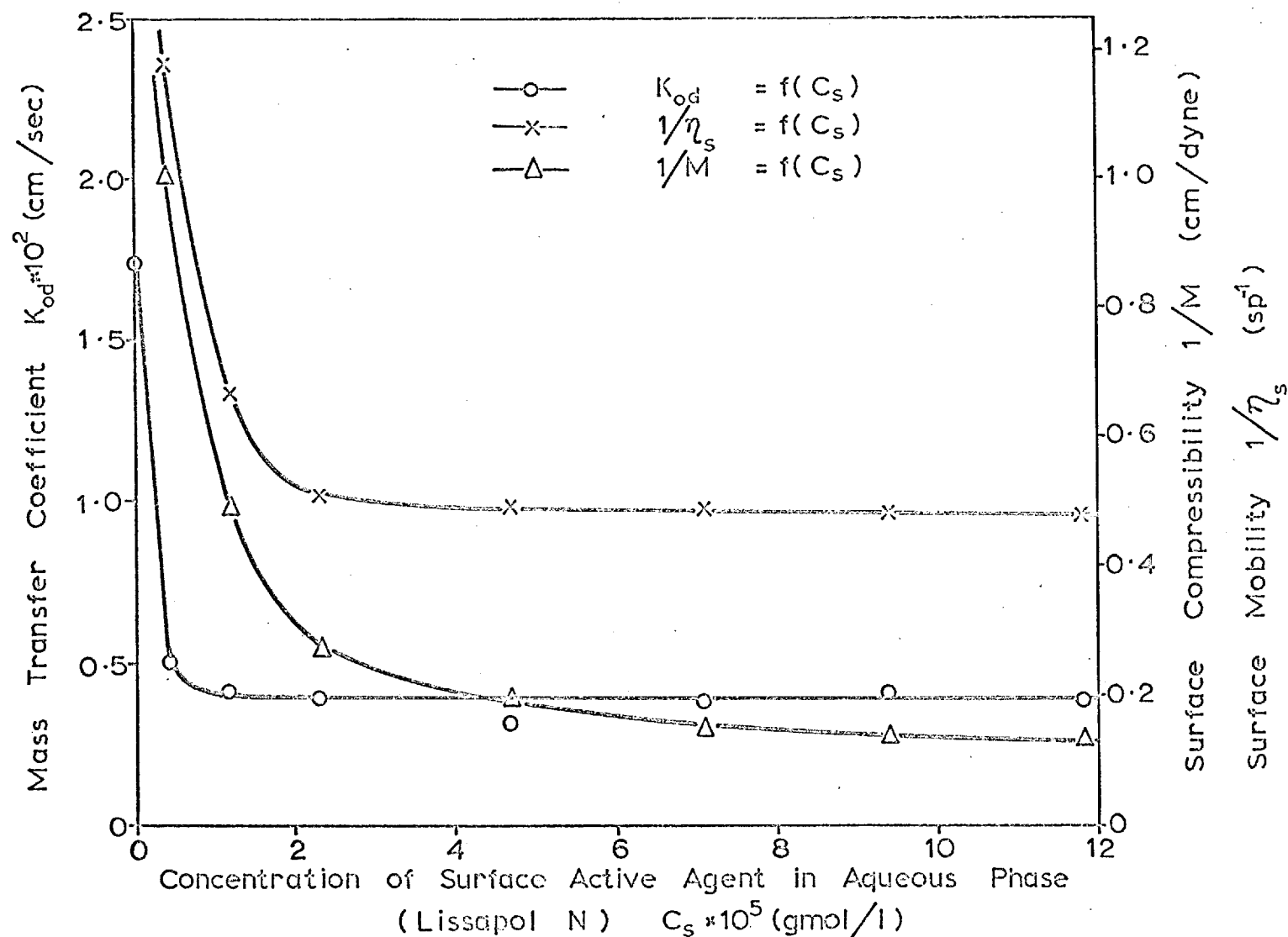


FIG. H.12 : MASS TRANSFER COEFFICIENT, SURFACE MOBILITY AND SURFACE COMPRESSIBILITY AS A FUNTION OF SURFACE ACTIVE AGENT CONCENTRATION

APPENDIX I

Surface Pressure Changes on the Basis of New Model

Run	C_B	C_W	C_{Wi}	C_{Bi}	σ_i^*	C_{Wi}'	$\sigma_i^{*'} $	$\Delta\pi'$	$K_{od} \cdot 10^2$	F
1	.496	0.0	0.69	.020	27.9	1.30	24.5	3.4	.994	2.37
2	.496	.249	.963	.031	26.2	1.57	23.2	3.0	.816	1.95
3	.496	.459	1.172	.045	25.2	1.78	22.3	2.9	.658	1.57
4	.496	.750	1.419	.063	23.9	1.97	21.5	2.4	.421	1.00
5	.487	.764	1.460	.066	23.7	1.98	21.4	2.3	.446	1.06
6	.477	1.019	1.700	.088	22.6	2.20	20.5	2.1	.414	.99
7	.496	1.030	1.718	.091	22.5	2.26	20.3	2.2	.409	.97
8	.471	1.264	1.934	.111	21.6	2.40	19.8	1.8	.556	1.32
9	.496	1.500	2.150	.134	20.7	2.65	18.9	1.8	.475	1.13
10	.492	1.509	2.160	.135	20.7	2.62	19.0	1.7	.403	.96
11	.496	1.825	2.460	.167	19.6	2.90	18.0	1.6	.380	.91
12	.496	2.103	2.720	.194	18.6	3.04	17.5	1.1	.421	1.00
13	.484	2.141	2.758	.198	18.5	3.10	17.3	1.2	.441	1.05
14	.485	2.645	3.223	.260	16.9	3.50	16.1	0.8	.431	1.03
15	.487	2.645	3.223	.260	16.9	3.50	16.1	0.8	.386	.92
16	.487	3.145	3.690	.325	15.6	3.86	15.2	0.4	.414	.99
17	.980	0.0	1.43	.062	23.9	2.60	19.0	4.9	1.710	4.07
18	.980	.226	1.67	.085	22.7	2.76	18.5	4.2	1.43	3.40
19	.980	.426	1.85	.100	22.0	2.95	17.8	4.2	1.30	3.10
20	.980	.604	2.01	.120	21.3	3.07	17.4	3.9	1.18	2.80
21	.980	.770	2.17	.136	20.7	3.15	17.1	3.6	1.10	2.62
22	.980	.975	2.35	.153	20.0	3.33	16.6	3.4	.95	2.26
23	.980	1.180	2.57	.179	19.2	3.51	16.0	3.2	.88	2.10
24	.980	1.398	2.74	.195	18.5	3.68	15.6	2.9	.83	1.98
25	.980	1.853	2.96	.223	17.8	3.86	15.1	2.7	.75	1.79
26	.980	2.240	3.51	.300	16.1	4.30	14.0	2.1	.66	1.57
27	.980	2.810	4.05	.379	14.5	4.76	13.0	1.5	.56	1.33
28	.987	3.293	4.50	.448	13.6	5.13	12.2	1.4	.416	.99
29	.980	3.774	4.94	.578	12.6	5.46	11.5	1.1	.387	.92

Appendix I (cont)

30	.964	4.195	5.35	.589	11.7	5.75	10.8	.9	.390	.93
31	.984	4.763	5.85	.681	10.7	6.17	10.0	.7	.402	.96
32	1.94	0.0	2.76	.196	18.5	4.85	12.8	5.7	2.00	4.76
33	1.94	.510	3.28	.269	16.7	5.22	12.0	4.7	1.72	4.69
34	1.94	1.12	3.69	.325	15.6	5.51	11.4	4.2	1.45	3.45
35	1.94	1.603	4.23	.403	14.2	5.92	10.5	3.7	1.25	2.97
36	1.94	2.205	4.76	.489	13.0	6.35	9.7	3.3	.951	2.26
37	1.94	2.617	4.94	.519	12.6	6.51	9.4	3.2	.802	1.91
38	1.94	3.720	6.21	.753	9.9	7.50	7.6	2.3	.584	1.39
39	1.96	4.234	6.71	.871	9.0	7.89	7.0	2.0	.399	.95
40	1.94	4.753	7.20	.991	8.2	8.27	6.6	1.6	.419	1.00

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Einfluß von Oberflächenerscheinungen auf die Stoffdurchgangszahlen bei der Flüssig-Flüssig-Extraktion

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Einfluß von Oberflächenerscheinungen auf die Stoffdurchgangszahlen bei der Flüssig-Flüssig-Extraktion*)

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Für den Stoffübergang in Flüssig-Flüssig-Systemen gibt es drei verschiedene Bereiche, die u. a. durch den Grenzflächendruck und die Oberflächenkompressibilität stark beeinflußt werden. Es werden quantitative Beziehungen zwischen den verfahrenstechnischen und physikalischen Größen in den drei Bereichen aufgestellt, sowie der Einfluß der Oberflächenerscheinungen auf die Stoffübergangszahlen und auf die Koaleszenz von Tropfen an ebenen Flächen und in einer Sprühkolonne untersucht.

Örtliche Unterschiede der Grenzflächenspannung haben bekanntlich eine Instabilität der Grenzfläche zur Folge, die sich dann als hydrodynamische Störung weiter fortpflanzt. Unterschiede in der Grenzflächenspannung können durch Temperatur- oder Konzentrationsschwankungen hervorgerufen werden, wie sie beim Wärme- oder Stoffübergang zwischen zwei fluiden Phasen auftreten.

In unseren Untersuchungen haben wir uns auf die bei der Flüssig-Flüssig-Extraktion vorkommenden Grenzflächenerscheinungen beschränkt. Die grundlegenden Vorarbeiten auf diesem Gebiet stammen von Sigwart und Nassenstein^{1,2)} sowie von Kroepelin und Neumann³⁻⁶⁾. Diese Forscher haben festgestellt, daß die hydrodynamischen Störungen sehr stark sein können; wegen ihres Aussehens hat man sie Eruptionen genannt. Man kann erwarten, daß solche Störungen die Oberflächenerneuerung beeinflussen und damit auch die Stoffdurchgangszahl vergrößern. Das Ziel dieser Arbeit ist, diesen Einfluß der Oberflächenerscheinungen zu untersuchen.

Qualitative Untersuchungen

In einer an einer anderen Stelle veröffentlichten Arbeit⁷⁾ wurde der Stoffübergang von Essigsäure aus einem Tetrachlorkohlenstoff- oder Benzoltropfen in Wasser qualitativ untersucht. Bei der in dieser Arbeit verwendeten Methode wurde am Ende eines Kapillarrohres schnell ein Tropfen gebildet und dann die Stoffzufuhr zur Tropfenphase abgeschnitten. Der Vorgang wurde in einem Schlierenfeld beobachtet. Es zeigte sich, daß der Stoffübergang in drei verschiedenen Bereichen stattfinden kann, die durch ihr Aussehen leicht zu unterscheiden sind. Wir haben diese Bereiche als turbulenten, eruptiven und Diffusionsbereich bezeichnet. Im Diffusionsbereich (Abb. 1) ist der Tropfen von einer Diffusionsschicht umgeben, die durch freie Konvektion stetig abgeführt wird. Im eruptiven Bereich (Abb. 2) wird diese Diffusionsschicht periodisch zerstört, während im turbulenten Bereich (Abb. 3) die Anzahl der Eruptionen so zunimmt, daß man kaum noch von individuellen Eruptionen sprechen kann. Statt dessen befindet sich die Grenzfläche laufend in einem stark turbulenten Zustand.

Quantitative Untersuchung des Stoffübergangs

Für die quantitative Untersuchung des Stoffübergangs in den drei Bereichen wurde eine Apparatur (Abb. 4) gebaut, die es ermöglichte, die Anzahl der Variablen klein zu halten. Sie bestand aus zwei gekoppelten Mikropumpen *a*, die durch die Kapillarrohre *b* mit einer Düse *c* verbunden waren. Ein dünnes Stahlrohr *d* wurde in ein Ka-

pillarrohr eingeführt und dort eingeschmolzen. Die eine Pumpe bildete den Tropfen durch die Ringspalte zwischen dem Kapillarrohr und dem Stahlrohr, und unter der Wirkung der zweiten Pumpe wurde der Tropfen dann zurückgezogen. Die Verdrängung der Pumpen wurde so eingestellt, daß der Tropfen seine kritische Größe nicht erreichte



Abb. 1. Stoffübergang im Diffusionsbereich.

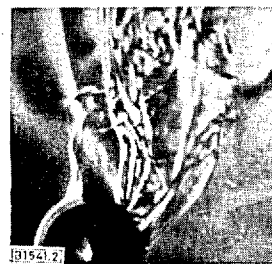


Abb. 2 (oben rechts). Stoffübergang im eruptiven Bereich.

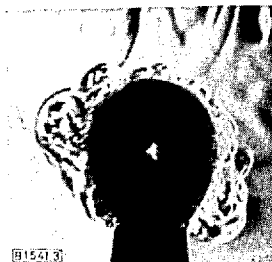


Abb. 3 (rechts). Stoffübergang im turbulenten Bereich.

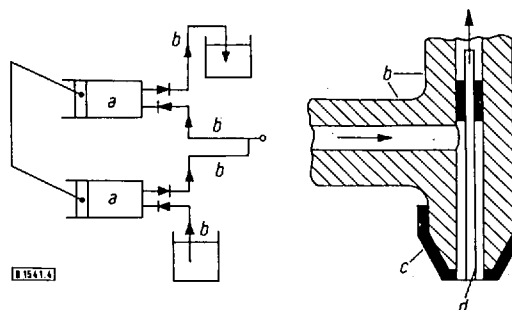


Abb. 4. Schema der Versuchsanlage.
a Mikropumpe, *b* Kapillarrohre, *c* Düse, *d* Stahlrohr

und die Tropfengröße daher von den physikalischen Eigenschaften der untersuchten Systeme unabhängig war. (Eine genaue Beschreibung der Versuchsanordnung wird demnächst erscheinen⁸⁾).

Als Tropfenphase wurde Benzol und als kontinuierliche Phase Wasser benutzt. Die gelösten Stoffe waren Essigsäure, Monochloressigsäure, Aceton und Phenol; die Richtung des Stoffüberganges war stets aus dem Benzol in das Wasser. Die Zuflußkonzentration in der Benzol-Phase wurde konstant gehalten und die Zuflußkonzentration des Gelösten im Wasser, und damit die treibende Kraft und die Grenzflächenspannung, geändert.

Die Resultate wurden als Stoffdurchgangszahlen berechnet und als Funktion der Konzentration des Gelösten im Wasser c_C aufgetragen. In Abb. 5 sind die Resultate für Phenol dargestellt. Die Zuflußkonzentration des Phe-

*) Vortrag des erstgenannten Autors auf dem Jahrestreffen der Verfahrens-Ingenieure vom 7. bis 10. Oktober 1962 in Mainz. In der Vortragsankündigung war die Bezeichnung „Stoffübergangszahlen“ verwendet worden. Die Stoffdurchgangszahl K_D wird auf die dispergierte Phase bezogen und ist durch folgende Gleichung definiert:

$$K_D \equiv \text{Massenstromdichte} / (c_D - m c_P).$$

Die Stoffübergangszahl in der Phase *D* ist gegeben durch den Ausdruck

$$k \equiv \text{Massenstromdichte} / (c_D - c_{Dg}).$$

m ist der Verteilungskoeffizient, c_{Dg} die Konzentration des Gelösten an der Grenzfläche.

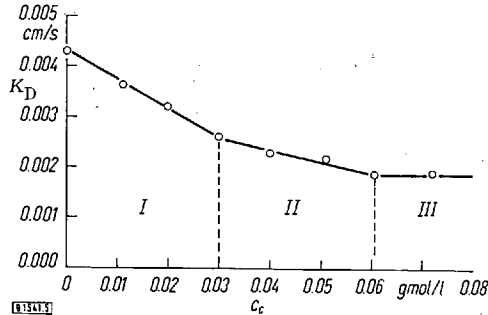


Abb. 5. Abhängigkeit der Stoffdurchgangszahl K_D von der Konzentration c_c des Phenols im Wasser bei einer konstanten Zuflußkonzentration von 1,78 gmol/l Phenol im Benzol.
I turbulenter Bereich, II eruptiver Bereich, III Diffusionsbereich.

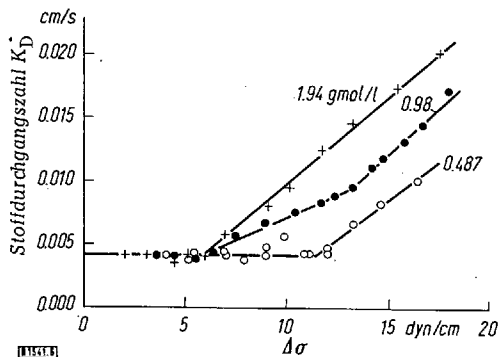


Abb. 6. Abhängigkeit der Stoffdurchgangszahl K_D von dem Grenzflächendruck $\Delta\sigma$ für das System Benzol/Essigsäure/Wasser für drei verschiedene Zuflußkonzentrationen von Essigsäure im Benzol.

nols im Tropfen war konstant und betrug 1,78 gmo/l. Ähnliche Resultate wurden mit Essigsäure und Chlor-essigsäure erhalten. Die drei Stoffübergangsbereiche sind deutlich zu unterscheiden. In Abb. 6 sind die Stoffdurchgangszahlen als Funktion des Grenzflächendrucks für drei verschiedene Zulaufkonzentrationen c_D von Essigsäure eingetragen. Daraus geht hervor, daß erst von einem gewissen Grenzflächendruck an, in diesem Falle 6 dyn/cm, die Stoffdurchgangszahl ansteigt. Der Grenzflächendruck wird hier als der Unterschied zwischen den Gleichgewichtsgrenzflächenspannungen definiert, welche den Zusammensetzungen an der Grenzfläche und im Tropfeninneren entsprechen. Die Verwendung dieser Größe setzt voraus, daß sich die Grenzflächeninstabilität schneller fortpflanzt, als sich das Gleichgewicht an der Grenzfläche einstellt. Die Veränderung der Stoffdurchgangszahl bei Anwesenheit von oberflächenaktiven Stoffen zeigt Abb. 7. Man erkennt, daß schon eine sehr kleine Menge von Teepol 514^{*)} (20 $\mu\text{mol/l}$) ausreicht, um den Stoffaustausch in den Diffusionsbereich zu verschieben. Die Stoffdurchgangszahl nimmt dann denselben Wert an wie im Diffusionsbereich, wenn keine oberflächenaktiven Stoffe vorhanden sind. Das ist ein Beweis dafür, daß die oberflächenaktiven Stoffe nur eine hydrodynamische Wirkung haben und den Stoffübergang direkt an der Oberfläche nicht behindern. Dies wurde bereits auf andere Weise durch Terjesen⁹⁾ gezeigt.

Die in Abb. 5, 6, und 7 gezeigten Ergebnisse stimmen in dem Bereich, in dem die Kurven flach verlaufen, ziemlich mit der Penetrationstheorie überein⁸⁾. Dagegen ist es viel schwieriger, eine Theorie für den Bereich des steilen Anstiegs zu finden. In diesem Bereich lassen sich die Stoffdurchgangszahlen weder als Funktion der treibenden Kraft noch als Funktion des Grenzflächendrucks in einer einzigen Kurve darstellen. Das ist auch nicht erstaunlich, da der Grenzflächendruck nur die treibende Kraft für die Fortpflanzung der Instabilitäten bildet und somit der Strömungswiderstand der Grenzfläche nicht erfaßt wird. Eine vollständige theoretische Behandlung des Fließverhaltens

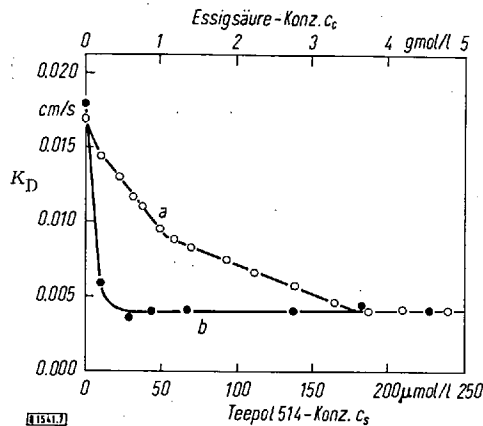


Abb. 7. Abhängigkeit der Stoffdurchgangszahl K_D von der Essigsäurekonzentration c_c im Wasser bei einer konstanten Zuflußkonzentration von $c_D = 0,98$ gmol/l Essigsäure im Benzol (Kurve a) und der Konzentration des oberflächenaktiven Stoffes Teepol 514 bei $c_D = 0,99$ gmol/l und $c_c = 0$ (Kurve b).

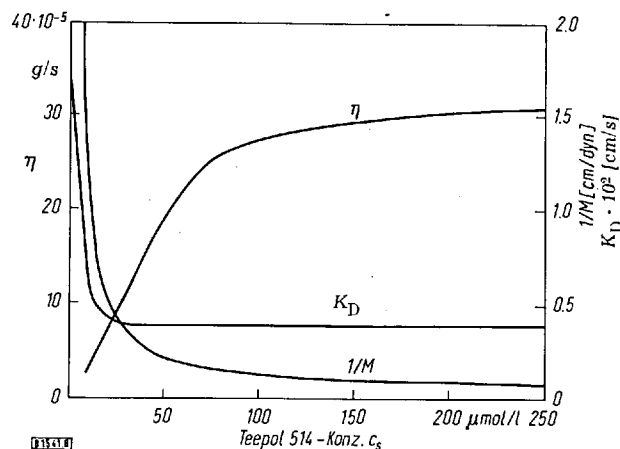


Abb. 8. Abhängigkeit der Stoffdurchgangszahl K_D , der Oberflächenscherzähigkeit η und der Oberflächenkompressibilität $1/M$ von der Konzentration des oberflächenaktiven Stoffes (Teepol 514).

an der Grenzfläche kann nur mit Hilfe der Navier-Stokes-Gleichung, in welche der Stoffübergang mit eingeführt wird, erreicht werden. Das ist aber wegen der komplexen Verhältnisse an der Grenzfläche kaum möglich.

Wir haben daher versucht, experimentell zu klären, welche von den beiden wichtigsten Oberflächeneigenschaften, die Oberflächenscherzähigkeit oder die Oberflächenkompressibilität, einen größeren Einfluß auf die Stoffdurchgangszahl ausübt. Dieses Problem wurde schon von Davies und Mayers¹⁰⁾ für unlösliche oberflächenaktive Stoffe, wie Eiweiß (Albumin) und Blutplasma, untersucht. Wir haben diese Untersuchung zuerst auf lösliche oberflächenaktive Stoffe, dann auf gelöste Stoffe im allgemeinen erweitert.

Die Oberflächenscherzähigkeit η wurde mit dem Ringspaltzähigkeitsmeter¹⁰⁾ gemessen. Die Oberflächenkompressibilität wurde durch den Modul der Kompressibilität M ausgedrückt

$$1/M = - \frac{1}{A} \frac{dA}{d\Delta\sigma} \quad (1),$$

wobei $\Delta\sigma$ der Grenzflächendruck und A die Oberflächengröße pro Molekül des grenzflächenaktiven Stoffes sind. A wurde mit Hilfe der Gibbsschen Absorptionsgleichung berechnet.

^{*)} WZ der Shell International Chemical Company Ltd., Waschmittel aus höheren sekundären Alkylsulfonaten.

Die Veränderung der Stoffdurchgangszahl, der Oberflächenscherzähigkeit und der Kompressibilität ist für Tee-pol 514® in Abb. 8 gezeigt. Die Krümmung der Zähigkeitskurve liegt bei 75 $\mu\text{mol/l}$ und die der Kompressionskurve bei 30 $\mu\text{mol/l}$. Die entsprechende Krümmung der Stoffdurchgangszahl erscheint bei 20 $\mu\text{mol/l}$. Ähnliche Resultate wurden mit Manoxol OT®^{***}, Dodecylaminhydrochlorid und Natriumlaurylsulfat als oberflächenaktive Stoffe erhalten. Diese Ergebnisse scheinen anzudeuten, daß beim Stoffübergang die Grenzflächenkompressibilität eine größere Rolle als die Grenzflächenscherzähigkeit spielt. Das stimmt mit den Ergebnissen von Davies und Mayers¹⁰) überein und wurde schon von Stuke¹¹) vorausgesagt.

Stoffübergangszahlen und Kennzahlen

Die Abhängigkeit des Stoffaustausches von den Grenzflächenerscheinungen bringt das Problem der Wiedergabe von Stoffübergangszahlen durch dimensionslose Kenngrößen erneut in den Vordergrund. Bekanntlich werden diese durch Potenzbeziehungen von der folgenden Form ausgedrückt:

$$\text{Sh}_D \sim \text{Re}_D^p \cdot \text{Re}_C^q \cdot \text{Sc}_D^r \quad (2a),$$

$$\text{Sh}_C \sim \text{Re}_D^s \cdot \text{Re}_D^t \cdot \text{Sc}_C^u \quad (2b).$$

Sh ist die Sherwoodsche Kennzahl, Re die Reynoldssche Kennzahl, Sc die Schmidtsche Kennzahl; der Index C verweist auf die kontinuierliche Phase, D auf die dispergierte Phase und p, q, r, s, t, u sind Konstanten. Da diese Beziehungen keine Grenzflächenparameter enthalten, können sie kaum von allgemeiner Bedeutung sein. Dasselbe gilt auch für den Einfluß des Diffusionskoeffizienten D auf die Stoffübergangszahl k .

In der Potenzbeziehung $k \sim D^n$ ist der Wert von n als 1 durch die Filmtheorie, als 0,5 durch die Penetrations-theorie¹²) und als 0 durch die hydrodynamische Theorie von Kischinewski¹³) gegeben. Die experimentell gefundenen Werte schwanken im Bereich von 0 bis 0,5¹⁴⁻¹⁷). Es ist möglich, daß diese Schwankungen durch die Vernachlässigung von Oberflächenerscheinungen hervorgerufen sind. Wenn man die Stoffübergangszahl in ihrer Danckwert-schen Form¹⁸) betrachtet, erhält man für den Übergang von Stoff A durch eines der Lösungsmittel bis zur Grenzfläche

$$k_A = (D_A s_A)^{1/2} \quad (3a)$$

und für Stoff B durch dasselbe Lösungsmittel

$$k_B = (D_B s_B)^{1/2} \quad (3b),$$

wobei k die Stoffübergangszahl und s die zeitliche Oberflächenenerneuerung bedeuten. Die Gln. (3a) und (3b) geben

$$k_A/k_B = (D_A/D_B)^{1/2} \cdot (s_A/s_B)^{1/2} \quad (4).$$

Es folgt daraus, daß in Dreikomponentensystemen der Einfluß des Diffusionskoeffizienten nur dann untersucht werden kann, wenn die Intensität der Oberflächenenerneuerung für jeden gelösten Stoff dieselbe ist. Im anderen Fall, unter der Annahme von

$$k_A/k_B = (D_A/D_B)^n \quad (5),$$

wird der physikalische Sachverhalt durch einen empirischen Potenzwert des Diffusionskoeffizienten nicht richtig dargestellt.

Die Geschwindigkeit der Oberflächenenerneuerung läßt sich für den Übergang von zwei Stoffen gleich groß halten, wenn man die gelösten Stoffe A und B gleichzeitig in verdünnte Lösungen überträgt. Der hydrodynamische Zustand an der Grenzfläche ist dann derselbe für beide Stoffe.

Wir untersuchten daher den Stoffübergang von Phenol und Propionsäure zwischen Tetrachlorkohlenstoff und Wasser in einer Gleichstromdünnschichtkolonne und in einer waagerechten Dünnschichtapparatur. Für Propion-

säure, eine stärkere Oberflächeninstabilität hervorruft, war die Stoffdurchgangszahl für den getrennten und für den gleichzeitigen Übergang dieselbe. Für Phenol war sie aber für den gleichzeitigen Übergang ungefähr um 25% größer als beim getrennten Austausch. Wenn diese Tatsache berücksichtigt wurde, konnten die in der senkrechten Kolonne und die in der waagerechten Apparatur erhaltenen Ergebnisse mit Hilfe der Danckwertsschen Oberflächenenerneuerungstheorie, d. h. unter der Annahme von $k \sim D^{1/2}$, erklärt werden¹⁹). Ein ausführlicher Bericht über diese Arbeit ist in Vorbereitung²⁰).

Koaleszenz an ebenen Flächen

Die Grenzflächeninstabilität beeinflusst nicht nur die Grenzflächenenerneuerung, sondern auch die Grenzflächen-größe und damit die volumetrischen Stoffdurchgangszahlen. In unserer Arbeit²¹) über den Einfluß des Stoffüber-gangs auf die Oberflächengröße haben wir uns zuerst auf die Koaleszenz an ebenen Flächen beschränkt, wobei die Koexistenzzeit der Tropfen an der Fläche gemessen wurde. Die Messungen wurden dann auf eine Sprühkolonne er-weitert.

Die Apparatur für die Messung von den Koexistenzzeiten ist in Abb. 9 dargestellt. Um kinetische Effekte klein zu halten, wurde der Tropfen sehr nahe an der Grenzfläche gebildet und ein System (Wasser/Kohlensäure-diäthylester) mit kleinem Dichteunterschied gewählt. Die Koexistenzzeit ohne Stoffübergang wurde als Bezugsgröße genommen. In Abb. 10 wurde für zwei Experimente (zusammen 400 Messungen) der Anteil F der Tropfen, die bis zur Zeit t koaleszierten, als Funktion der Koexistenzzeit

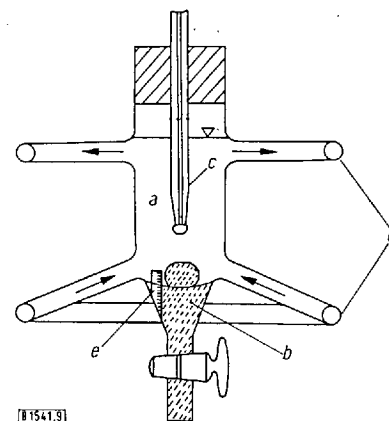


Abb. 9. Apparatur für die Messung von Koexistenzzeiten: a kontinuierliche Phase; b dispergierte Phase (Tropfenphase); c Kapillarrohr; d Glasröhre für den Ein- und Ausfluß der kontinuierlichen Phase; e Maßstab für die Konstanthaltung des Grenzflächenniveaus.

(Ruhezeit an der Grenzfläche) aufgetragen. Die Zeit, für welche $F = 0,5$ ist, wurde die mittlere Koexistenzzeit $\bar{t}$ genannt. Die Gradienten dieser Kurven stellen die Verteilungskurve der Koexistenzzeiten dar (Abb. 11). Die Zeit, welche dem Maximum einer Kurve entspricht, ist die wahrscheinliche Zeit der Koaleszenz t_p .

Für die Abhängigkeit von t_p von der Tropfengröße ergab sich, daß die wahrscheinliche Zeit der Koaleszenz dem äquivalenten Durchmesser des Tropfens zur fünften Potenz proportional ist. Dieses Ergebnis ist in Übereinstimmung mit der Gleichung für die Filmdicke h während der Annäherung von zwei parallelen Scheiben²²)

$$1/h^2 = 1/H^2 + 16\pi^2 (\rho_D - \rho_C) g r^3 t / (\mu_C A_c^2) \quad (6),$$

wenn man in dieser Gleichung für die Kontaktfläche A_c die durch Derjaguin und Kusakow²³) für Luftblasen ermittelte Beziehung

$$A_c = 8\pi r^4 (\rho_D - \rho_C) g / \sigma \quad (7)$$

einsetzt. In den Gln. (6) und (7) ist H die Integrationskonstante ($h = H$ bei $t = 0$); ρ_D und ρ_C sind die Dichten

*** WZ der Firma Hardman & Holden, Manchester, Netzmittel aus Natriumdinonylsulfosuccinat.

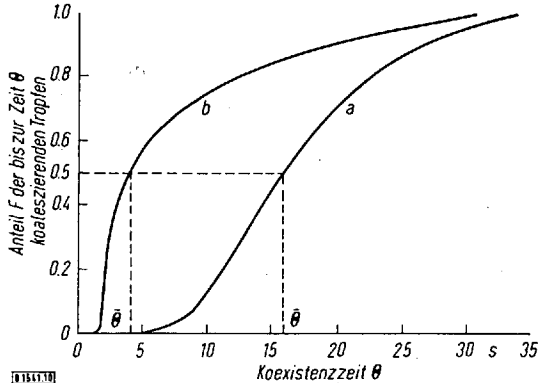


Abb. 10. Verteilung der Koexistenzzeiten.

	Kurve a	Kurve b
kontinuierliche Phase	H ₂ O	H ₂ O mit 1 Tropfen Teepol 514 pro 1
dispergierte Phase	OC(OC ₂ H ₅) ₂	0,46 n C ₂ H ₅ COOH in OC(OC ₂ H ₅) ₂
Tropfengröße [ml]	0,44	0,42
Anzahl der gebildeten Tropfen N ₀	300	100

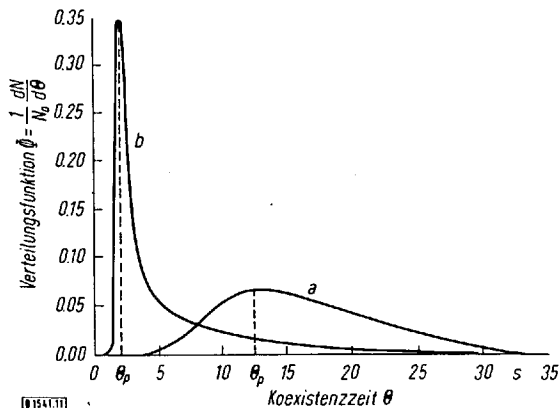


Abb. 11. Verteilungskurve der Koexistenzzeiten.
Kurven a und b wie bei Abb. 10.

der dispergierten und kontinuierlichen Phasen, r ist der äquivalente Radius des Tropfens; t bedeutet die Zeit; σ ist die Grenzflächenspannung, und μ_C ist die Zähigkeit der Filmphase.

Aus photographisch ermittelten Werten von H und A_0 wurde in 30 Experimenten, in denen der äquivalente Radius von 2,5 bis 5,5 mm geändert wurde, die theoretische Filmdicke für die wahrscheinliche Zeit der Koaleszenz berechnet. Die Ergebnisse zeigten eindeutig, daß es eine wahrscheinliche Filmdicke gibt, bei welcher der Film reißt. Unter den untersuchten Bedingungen betrug diese $9 \pm 0,3 \mu$ und war von der Tropfengröße unabhängig. Der Krümmungsradius des Films war ziemlich groß, so daß die Annahme von ebenen Flächen keinen großen Fehler verursachen konnte. Bei diesen Beobachtungen wurde angenommen, daß der Tropfen starr ist. In Wirklichkeit ist eine schwache Zirkulation vorhanden, wodurch die Filmdicke ungefähr auf $8,3 \mu$ erniedrigt wird. Ewers und Sutherland²⁴⁾ haben gezeigt, daß erst bei einer Filmdicke kleiner als 50 Å die molekulare Bewegung als Ursache für das Zerreißen in Frage kommt. Man kann darum vermuten, daß Kapillarwellen an dem Prozeß teilnehmen, wie es bereits Gillespie und Rideal²⁵⁾ angenommen haben.

Der Einfluß oberflächenaktiver Stoffe und des Stoffübergangs auf die Koaleszenz ist aus Tab. 1 ersichtlich. Der Stoffübergang in der Richtung vom Tropfen zur konti-

Tabelle 1. Koaleszenz an der Grenzfläche Wasser/Kohlensäurediäthylester

Dispergierte Phase	Kontinuierliche Phase	Mittlere Koexistenzzeit (s)	
		ohne oberflächenaktiven Stoffen	mit oberflächenaktiven Stoffen
OC(OC ₂ H ₅) ₂	H ₂ O	16	42*
0,5 n C ₂ H ₅ COOH in OC(OC ₂ H ₅) ₂	H ₂ O	0,2	3,7*
OC(OC ₂ H ₅) ₂	0,5 n C ₂ H ₅ COOH in H ₂ O	66	230*
H ₂ O	OC(OC ₂ H ₅) ₂	4,8	
0,5 n C ₂ H ₅ COOH in H ₂ O	OC(OC ₂ H ₅) ₂	0,5	
0,5 n CH ₃ COOH in H ₂ O	OC(OC ₂ H ₅) ₂	1,0	7,5**

* 1 Tropfen Teepol 514 pro 1

** 1 Tropfen 0,03 m Dodecylaminhydrochlorid pro 1

nuierlichen Phase verkleinert die Koexistenzzeit (beinahe momentane Koaleszenz), während der Stoffübergang in der anderen Richtung die Koexistenzzeit stark vergrößert. Diese Ergebnisse können durch die Grenzflächeninstabilitäten leicht erklärt werden. Im ersten Fall wird das Abfließen des Films durch die Grenzflächenvorgänge erleichtert, und im zweiten Fall erschwert^{26,27)}. Die oberflächenaktiven Stoffe erhöhen, wie erwartet, die Koexistenzzeit.

Koaleszenz in einer Sprühkolonne

Ergebnisse, die den an ebenen Flächen gewonnenen ähnlich sind, wurden in einer Sprühkolonne erhalten. Die mit 4 Düsen ausgestattete Sprühkolonne hatte eine Länge von 72 cm und einen Durchmesser von $4\frac{3}{4}$ cm. Die Koaleszenz wurde durch die folgende Beziehung definiert

$$\% \text{ Koaleszenz} = \frac{\text{Anzahl der (gebildeten — koaleszierenden) Tropfen} \times 100}{\text{Anzahl der gebildeten Tropfen}} \quad (8).$$

In dieser Beziehung ist die Anzahl der koaleszierenden Tropfen durch die Anzahl der Tropfen, die an der oberen Grenzfläche angelangt sind und dort koaleszierten, ausgedrückt. Die Tropfenzahlen wurden durch Filmaufnahmen bestimmt. Die Ergebnisse (Tab. 2) sind in qualitativer Übereinstimmung mit der Koaleszenz an ebenen Flächen.

Tabelle 2. Koaleszenz in einer Sprühkolonne

Dispergierte Phase	Kontinuierliche Phase	% Koaleszenz	
		ohne oberflächenaktiven Stoffen ⁺	mit oberflächenaktiven Stoffen ⁺
Benzol	Wasser	32	2,5
Benzol	0,64 n C ₂ H ₅ COOH in H ₂ O	1,2	0
0,26 n C ₂ H ₅ COOH in C ₆ H ₆	Wasser	43	3

⁺ 3 Tropfen Teepol 514 pro 1

Zusammenfassung

Die qualitativen Untersuchungen über den Einfluß von Oberflächenercheinungen auf den Stoffübergang bei der Flüssig-Flüssig-Extraktion haben gezeigt, daß es drei hydrodynamisch verschiedene Bereiche für den Stoffübergang gibt. In dem Diffusionsbereich, der stabil und von Konzentrationsänderungen unabhängig ist, können die Stoffdurchgangszahlen vorausberechnet werden. Sobald aber der Grenzflächendruck eine kritische Größe erreicht, die für das System Benzol/Essigsäure/Wasser ungefähr 6 dyn/cm beträgt, wird die Grenzfläche instabil, und die Stoffdurchgangszahlen steigen an. In diesen instabilen Bereichen, die als eruptiv und turbulent

bezeichnet wurden, sind die Verhältnisse so kompliziert, daß kein einfacher Zusammenhang zwischen den Stoffdurchgangszahlen und den physikalischen Parametern gefunden wurde. Die Ergebnisse, welche bei Anwesenheit oberflächenaktiver Stoffe erhalten wurden, scheinen aber anzudeuten, daß der Grenzflächendruck und die Oberflächenkompressibilität dort von maßgebender Bedeutung sind. Die Abhängigkeit des Stoffübergangs von den Oberflächenerscheinungen zeigt, daß Gleichungen zur Berechnung von Stoffübergangszahlen nur dann eine allgemeine Gültigkeit haben können, wenn sie Oberflächenparameter enthalten. Wenn das nicht der Fall ist, haben die Potenzen von verschiedenen physikalischen und verfahrenstechnischen Größen kaum eine physikalische Bedeutung. Die Oberflächeninstabilität beeinflusst nicht nur den Stoffübergang, sondern auch die Oberflächengröße und damit die volumetrischen Stoffdurchgangszahlen. Die Koaleszenz von Tropfen an einer ebenen Fläche und auch in einer Sprühkolonne verläuft viel schneller, wenn gleichzeitig ein Stoffübergang von der dispergierten in die kontinuierliche Phase stattfindet und viel langsamer, wenn der Stoff in die andere Richtung übergeht. Auch die Anwesenheit oberflächenaktiver Stoffe spielt eine wichtige Rolle bei der Verhinderung von Koaleszenz.

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