Studies on the behaviour of some mono-carboxylic acids at the solution-vapour interface

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How to cite:

Akhtar, B. A. (1968) *Studies on the behaviour of some mono-carboxylic acids at the solution-vapour interface*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/10012/

STUDIES ON THE BEHAVIOUR OF SOME MONO-CARBOXYLIC ACIDS AT THE SOLUTION-VAPOUR INTERFACE

being

a Thesis submitted to

The University of Durham

For

The Fulfilment of the Requirements

For

The Degree of

Master of Science

By

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Fourah Bay College,

Freetown.

March,1968.

STUDIES ON THE BEHAVIOUR OF SOME MONO-CARBOXYLIC ACIDS AT THE SOLUTION-VAPOUR INTERFACE

B. A. AKHTAR, FOURAH BAY COLLEGE, FREETOWN

The behaviour of acetic, propionic and butyric acids at the solution-vapour interface at 30° has been studied systematically. The surface tensions and vapour-pressures of fourteen systems were measured and the Gibbs adsorption equation used to calculate surface excesses, Γ^{n}, whilst the amounts of the individual components at the interface were calculated by well-known methods. It is assumed that the thickness of the adsorbed phase is essentially monolayer in character. The orientation of the acids at the interface is assumed to be the 'parallel' one for adsorption from benzene, carbon tetrachloride and cyclohexane and the 'perpendicular' one for adsorption from ethyl alcohol and water. Two factors, - affinity between acid and solvent in the bulk and rate of lowering of surface tension of acid + solvent mixtures by the acids, have been used to account for the extent of acid adsorption at the interface.

In general adsorption of acid increases with increasing chain length, although for the cyclohexane systems it decreases with increasing acid chain length. The occurrance of a mixed monolayer at the interface is observed for all the systems, and a uni-monolayer of acid is formed only from the pure component.

For the water systems it is possible for the adsorbed layer to contain two water molecules along the length of the acid molecule due to the much smaller size of the water molecule.

The present investigations have thrown further light

on adsorption behaviour at the solution-vapour interface. A complete understanding of adsorption phenomenon at the interface, involving a reasonable assessment of thickness of the adsorbed layer, composition and orientations at the interface, etc., depends on the particular systems involved, on the properties of the solutions, and on the intermolecular interactions possible both in bulk solution and at the interface.

The work described in this thesis was carried out in the Physical Chemistry Research Laboratory at Fourah Bay College, the University College of Sierra Leone.

ACKNOWLEDGEMENT

I wish to express my thanks to Dr. E.H.M. Wright, B.Sc., Ph.D., A.R.I.C., of the Chemistry Department, Fourah Bay College, University of Sierra Leone, for his guidance, help and advice throughout this investigation, and to Professor S.R.Landor, D.Sc. Ph.D., D.I.C., F.R.I.C., head of the Chemistry Department during the period of my research, for constant encouragement and for making possible the provision of ample equipment and apparatus.

I am indebted to the Sierra Leone Oxygen Factory at Kissy Dock Yard, Freetown for free supply of liquid oxygen, to Mr. A.E.Harris, the Chief Technician for his help and advice in the construction of various apparatus, and to Fourah Bay College for providing the overall research facilities.

B. A. AKHTAR.

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INTRODUCTION

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CHAPTER 1.

GENERAL INTRODUCTION.

Adsorption is an important phenomenon which occurs at interfaces. This term is used to describe the phenomenon associated with the existence of a higher concentration of a substance at the surface of a liquid or solid than is present in the bulk phase. Studies on the structure of the surface layer of solutions is an important topic in this century and such studies are generally pursued by indirect methods, which may involve the application of the Gibbs adsorption equation to surface tension and activity data.

Adsorption from solutions may be studied at different interfaces viz liquid-liquid, liquid-vapour and liquid-solid. Of these the first two are, in principle, the simplest, because the use of pure substances gives a homogeneous adsorbed phase. However, the majority of workers have paid special attention to the last interface and much less work has been reported on the first two interfaces. In the present work the systems chosen consist of completely miscible binary liquids and an attempt is made to study the nature and composition of the liquid-vapour interface.

The surface energy of a pure liquid consisting of one species of molecule tends to be minimised by the diminution of the total surface to the minimum possible, and molecules leave the surface for the interior under the action of inward attractive forces exerted on the surface molecules. In the case of solutions of two or more substances, the molecules which have the greater fields of force tend to pass into the interior and those with the smaller fields remain at or near the surface. As a result of this tendency of the free energy of the surface to decrease, a solute having a lower surface tension will tend to concentrate on the surface. This concentration of one component of a solution at the surface is called adsorption. If there is an increase of concentration of one component of a solution at the surface then the adsorption is positive and in the case of a decrease in concentration, the adsorption of that component is negative.

Qualitatively the rule for adsorption is that, if the solution has a smaller surface tension than the solvent, the solute is concentrated at the surface, and if it has a larger surface tension, the solute is driven as far as possible into the interior.[1]

Gibbs deduced the quantitative relation between the amount of adsorption and the change in surface tension[2]. The Gibbs adsorption equation may be written in the form

$$\Gamma_2 = -\frac{1}{RT}\frac{\partial \gamma}{\partial \ln a_2}, \qquad \text{----------} \qquad (1)$$

Where Γ_2 is excess concentration of the solute per square cm. of surface as compared with that in the bulk of the solution, γ is the surface tension of the solution, a_2 is the activity of the solute, R is the gas constant and T the absolute temperature. According to this equation, if a solute causes a decrease in surface tension of the solvent, $\frac{\partial \gamma}{\partial \ln a_2}$ will be negative, and adsorption of the solute will be more at the surface. Similarly if the solute causes an increase in surface tension of the solvent, $\frac{\partial \gamma}{\partial \ln a_2}$ will be positive, and adsorption of the solute will be less at the surface, Different workers, for example

Gurwitsch[3], Harkins & Wampler[4], Belton[5] and Kipling[6] have used the above equation in the study of the liquid-vapour interface and their results agree, in general, with the requirements of equation (1).

Harkins and Wampler[4] used the form of Gibbs equation which gives the surface excess as Γ_2. Guggenheim and Adam[7] pointed out that Γ_2 could be calculated according to different conventions and the surface excess calculated had correspondingly different values. The surface excess for unit area of surface denoted by Γ_2 is the excess of the solute in the surface layer over the number of moles of solute in that part of the bulk region containing the same number of moles of solvent.

Surface tension values are necessary in order to be able to calculate surface excess. According to the Gibbs equation the surface tension change is responsible for the change in the surface excess values. The second important requirement for calculating surface excess is activity data.

In the present work the surface excess for some systems have been determined with the help of surface tension and activity data, and the individual amounts of each of the components at the interface are deduced by well-known methods.[6] The variation of acid adsorption with chain length and with solvent is then discussed.

CHAPTER 2

Theoretical Approaches to the Subject.

The Surface Excess.

There are two concepts of adsorption as applied to mixtures. The first, applied to adsorption from a mixture of several components, is referred to as preferential or selective adsorption[8], and the measured adsorption corresponds to a surface excess. This is a measure of the extent to which the bulk liquid is impoverished with respect to one component as the surface layer is correspondingly enriched. The second is the true adsorption of an individual component, and refers to the actual quantity of that component present in the adsorbed phase.

Adsorption at the liquid-vapour phase boundary is considered to be mainly due to physical forces and this has been an implicit assumption in the theoretical treatment of such systems. Solids, however, are known to adsorb gases chemically, even at low temperatures, and both chemisorption and physical adsorption may occur in the same system in adsorption from solutions on to solid surfaces.[9] For electrolytes which consists of ions which are bulky in size adsorption may be considered to be governed essentially by Van der Waals' forces because the ion is large in relation to the magnitude of its charge.[10]

The thermodynamic treatment of adsorption began effectively with the Gibb's equation which has been an essential feature of the treatment of the liquid-vapour and the liquid-liquid interfaces. Gibbs treatment compares the actual system with a physically impossible system in which two layers touch without any transitional layer. Let us consider a solution with α and β as the upper and lower phases to the transitional region. A normal to the surface is moved round so as to enclose a volume of cross-section A perpendicular to the surface. The volume may (Fig. A)

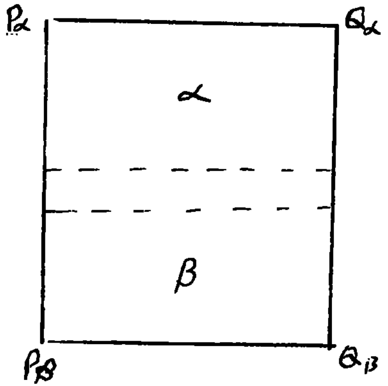


Fig. A

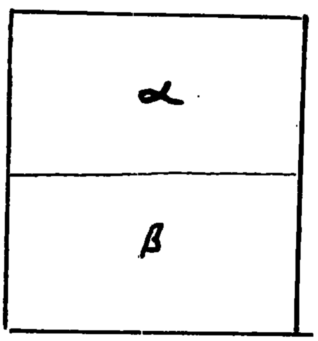


Fig. B

be finally defined by drawing surfaces $P_\alpha Q_\alpha$ and $P_\beta Q_\beta$ parallel to the physical surface. Next we may consider an idealized volume of the same length and cross-section in which the two phases are separated not by an actual physical surface but by a mathematical plane,(Fig B). $\Gamma_1, \Gamma_2 \ldots \Gamma_i$ may be regarded as the surface excesses of components 1,2, ...i, respectively, per unit area $\overset{s}{m}_1, \overset{s}{m}_2 \ldots \overset{s}{m}_i$ (where $\overset{s}{m}_i = A\Gamma_i$) for the surface excesses in the whole area A considered.

Now there is a difference in the amount of energy and of entropy between the actual and the idealized system. The excess of energy in the first over the second system may be taken as $\overset{s}{\epsilon}$ and the excess of entropy $\overset{s}{\eta}$ per unit area $\epsilon_s + \eta_s$ where $\overset{s}{\epsilon} = A\epsilon_s$. The energy of the system may be expressed as a sum of terms, each of which is the product of a capacity factor and an intensity factor. Taking entropy η, volume V, area A and amounts of the components m_i, as the capacity factors, and choosing temperature, pressure, surface tension and chemical potentials, $\mu_1, \mu_2, \mu_2 \ldots\ldots \mu_i$, as the intensity factors, the increase in energy of the actual system in any small reversible change when in equilibrium is given by the equation;

$$d\epsilon = Td\eta - p^{\alpha}dV^{\alpha} - p^{\beta}dV^{\beta} + \gamma dA + \mu_1 dm_1 + \dots + \mu_i dm_i \quad (2)$$

The increase of energy of each phase of the idealized system, separately, is given as:

$$d\epsilon^{\alpha} = Td\eta^{\alpha} - p^{\alpha}dV^{\alpha} - \mu_1 dm_1^{\alpha} + \mu_2 dm_2^{\alpha} + \dots + \mu_i dm_i^{\alpha} \quad (3)$$

$$d\epsilon^{\beta} = Td\eta^{\beta} - p^{\beta}dV^{\beta} - \mu_1 dm_1^{\beta} + \mu_2 dm_2^{\beta} + \dots + \mu_i dm_i^{\beta} . \quad (4)$$

But by the definition of surface excess

$$\epsilon^{s} = \epsilon - \epsilon^{\alpha} - \epsilon^{\beta} , \quad - - - - (5)$$

$$\eta^{s} = \eta - \eta^{\alpha} - \eta^{\beta} , \quad - - - - (6)$$

$$m_i^{s} = m_i - m_i^{\alpha} - m_i^{\beta} . \quad - - - - (7)$$

Subtracting equations (3) and (4) from (2), we have

$$d\epsilon^{s} = Td\eta^{s} + \gamma dA + \mu_1 dm_1 + \mu_2 dm_2 + \text{------} + \mu_i dm_i^{s} \ . \ - - - (8)$$

Since equation (8) is a homogeneous function of the first degree it may be integrated to

$$\epsilon = T\underline{d\eta}^{s} + \gamma A + \mu_1 m_1^{s} + \mu_2 m_2^{s} + \dots + \mu_i m_i^{s} \quad - - - (9)$$

which is an operation corresponding physically to a finite increase of area without change of composition.

Differentiating equation (9), one obtains

$$d\epsilon^s = T\,d\eta^s + \eta^s dT + \gamma\, dA + A\,d\gamma + \mu_1 dm_1^s + m_1 d\mu_1 + \cdots + \mu_i dm_i + m_i d\mu_i \quad (10)$$

and comparing (10) with (8) we have

$$A d\gamma = -\eta dT - m_1^s d\mu_1 - \ldots\ldots\ldots - m_i^s d\mu_i \quad . \quad (11)$$

For unit area of surface,

$$d\gamma = -\eta_s dT - \Gamma_1 d\mu_1 - \ldots\ldots\ldots - \Gamma_i d\mu_i \quad . \quad (12)$$

Equation (12) is the general form of the Gibbs relation between surface tension, temperature, surface excesses, and chemical potentials for a system of any number of components. At constant temperature and for systems of two components equation (12) becomes

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 . \quad - \; - \; - \quad (13)$$

If the mathematical plane between the two phases is fixed <u>then</u> the surface excess of component 1 vanishes and we get

$$d\gamma = -\Gamma_2^{(1)} d\mu_2 \quad - \; - \; - \quad (14)$$

If the activity coefficient of second component is f_2 and its mole fraction N_2 then

$$d\gamma = -RT\,\Gamma_2^{(1)} d\mu_2 \quad . \quad - \; - \; - \quad (15)$$

But

$$\mu_i = \mu_i^o + RT \log_e f_i N_2'' \; ; \quad - \; - \; - \quad (16)$$

hence

$$d\gamma = -RT\,\Gamma_2' \, d \log_e f_2 N_2 \; , \quad - \; - \; - \quad (17)$$

or

$$\Gamma_2^{(1)} = -\frac{1}{RT} \frac{d\gamma}{d \ln f_2 N_2} , \quad - \; - \; - \quad (18)$$

or $$\Gamma_2^{(1)} = -\frac{f_2N_2}{RT}\frac{\partial\gamma}{\partial(f_2N_2)} \qquad (19)$$

If component 2 is volatile and its vapour pressure obeys the perfect gas laws with sufficient exactness, the partial pressure in the vapour being p_2,

$$\Gamma_2^{(1)} = -\frac{p_2}{RT}\frac{\partial\gamma}{\partial N_2} \qquad (20)$$

For ideal solutions, with activity coefficient unity, equation (19) becomes

$$\Gamma_2^{(1)} = -\frac{N_2}{RT}\frac{\partial\gamma}{\partial N_2} \qquad (21)$$

For dilute and ideal solutions where the concentration c_2 is proportional to mole fraction and $f_2 = 1$ (22)

$$\Gamma_2^{(1)} = -\frac{c_2}{RT}\frac{\partial\gamma}{\partial c_2} \qquad (22)$$

Guggenheim and Adam have discussed various alternative definitions of Γ, made by fixing the mathematical surface of an idealized system in different ways[7]. The different conventions considered are discussed below.

<u>Convention (1)</u> Gibbs choice of fixing the mathematical surface so that Γ_1 vanishes, means that a portion of the liquid containing unit area of surface contains $\Gamma_i^{(1)}$ moles of each species more than a portion in the interior which contains exactly the same number of molecules of species 1. This may be called convention 1. The value of the

Corresponding to this convention will be specified as

$$\Gamma_i^{(1)} = 0 \quad . \quad - \quad - \quad - \quad - \qquad (23)$$

Similarly if we define Γ_i as the excess number of moles of the species i in a portion of liquid with unit surface area over a portion in the interior containing exactly the same number of moles of the species. 2, then the notation used is $\Gamma_i^{(2)}$ and is referred as convention 2.

$$\Gamma_i^{(2)} = 0 \quad . \quad - \quad - \quad - \quad - \qquad (24)$$

A general and precise form the Gibbs equation is[12]

$$- d\gamma = \sum_i \Gamma_i \, d\mu_i = \sum_i \Gamma_i \, d \ln a_i \quad - \quad - \quad - \qquad (25)$$

and for a two component mixture;

$$-d\gamma = \Gamma_1 \, d\mu_1 + \Gamma_2 \, d\mu_2 \quad - \quad - \quad - \quad - \quad - \qquad (26)$$

d (13)

whence, from the Gibbs - Duhem equation

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \quad - \quad - \quad - \quad - \qquad (27)$$

we have

$$d\gamma = \Gamma_1 \frac{x_2 \, d\mu_2}{x_1} - \Gamma_2 \, d\mu_2 , \quad - \quad - \quad - \qquad (28)$$

or

$$\frac{x_1 \, d\gamma}{d\mu_2} = \Gamma_1 x_2 - \Gamma_2 x_1 . \quad - \quad - \quad - \quad - \qquad (29)$$

Also

$$\frac{x_2 \, d\gamma}{d\mu_1} = \Gamma_2 x_1 - \Gamma_1 x_2 . \quad - \quad - \quad - \qquad (30)$$

Where $\frac{x_2 \, d\gamma}{d\mu_1}$ has the significance of surface excess.

Now keeping in view the convention 1 we have for a two component mixture

$$\Gamma_2^{(1)} = \Gamma_2 - \frac{x_2}{x_1}\Gamma_1 \quad ---- \quad (31)$$

or

$$\Gamma_2^{(1)} = \frac{1}{x_1}\left[\Gamma_2 x_1 - \Gamma_1 x_2\right]. \quad --- \quad (32)$$

Thus

$$\Gamma_2^{(1)} = +\frac{1}{x_1}\frac{x_2\,d\gamma}{d\mu_1} \quad -- \quad (33)$$

or

$$\Gamma_2^{(1)} = -\frac{d\gamma}{RT\,d\ln a_2} \quad . \quad --- \quad (34)$$

<u>Convention N</u> For comparison of different interfaces this convention is probably the most useful . $\Gamma_i^{(N)}$ is the excess of component i in the surface layer of unit area compared with the amount present in the quantity of bulk liquid which contains the same total number of moles of all species. Thus for a two component mixture we have

$$\Gamma_2^{(N)} = \Gamma_2 - x_2\left(\Gamma_1 + \Gamma_2\right) \quad --- \quad (35)$$

or

$$\Gamma_2^{(N)} = \Gamma_2 x_1 - \Gamma_1 x_2 \quad --- \quad (36)$$

or

$$\Gamma_2^{(N)} = \frac{x_2\,d\gamma}{d\mu_1}, \quad --- \quad (37)$$

or

$$\Gamma_2^{(N)} = \frac{x_1\,d\gamma}{d\mu_2}, \quad --- \quad (38)$$

or

$$\Gamma_2^{(N)} = \frac{-x_1\,d\gamma}{RT\ln a_2} = x_1\Gamma_2^{(1)} \quad -- \quad (39)$$

Where γ is the surface tension of solution, a_2 is the activity of component 2 and x_1 is the mole fraction of component 1.

✓

Con~~t~~ention M

Here Γ_i is defined as the number of moles of the species i in a portion of the liquid contained in unit area of the surface more than in a portion in the interior of exactly the same mass. Thus for a two component mixture:

$$\Gamma_2^{(M)} = \frac{-\Gamma_1 M_1 + \Gamma_2 M_2}{x_1 M_1 + x_2 M_2} x_2 \,, \quad - - - \qquad (40)$$

or

$$\Gamma_2^{(M)} = \frac{M_1}{M_2}\left(x_1 \Gamma_2 - x_2 \Gamma_1\right), \quad - - - \qquad (41)$$

where M_1 and M_2 are the molecular weights of component 1 and 2, respectively, and $\bar{M}$ is the mean molecular weight of the solution. Then

$$\Gamma_2^{(M)} = -\frac{M_1}{\bar{M}} \frac{x_1 d\gamma}{RT d\ln a_2} \,. \quad - - \qquad (42)$$

Convention V

Here Γ_i is denoted as the number of moles of the species i in a portion of the liquid contained in unit area of surface more than in a portion in the interior of exactly the same volume. Thus for a two component mixture:

$$\Gamma_2^{(V)} = \frac{V_1}{\bar{V}} \frac{x_1 d\gamma}{RT d\ln a_2} \quad - - - \qquad (43)$$

where V_1 and $\bar{V}$ are the partial molar volume of component 1 and the mean partial molar volume of the solution, respectively. The relationship between the surface excesses calculated according to the different conventions is given below:

$$\Gamma_2^{(N)} = x_1 \Gamma_2^{(1)} = \frac{m}{m_1} \Gamma_2^{(M)} = \frac{V}{V_1} \Gamma_2^{(V)} . \quad (44)$$

It is only with convention V that the geometrical surface coincides with the physical boundary of the liquid.

Nature of the adsorbed layer.

Once the surface excess has been calculated it is possible to get the actual surface concentrations for each component. In the present work convention N has been used to calculate the surface excess as it is the most useful convention for the comparison of different interfaces. $\Gamma_2^{(N)}$ is represented by the equation (39). For a liquid-solid interface the surface excess is given by the equation[10]

$$\frac{n_0 \Delta x}{m} = n_1^s x_2 - n_2^s x_1 . \quad --- \quad (45)$$

Where m is the weight of adsorbent brought into contact with n_0 moles of liquid. Δx respresents the change in mole fraction of the liquid with respect to component 1, n_1^s and n_1^s are the number of moles of component 1 and 2 respectively, transferred onto the surface of unit weight of solid, x_1 and x_2 refer to the equilibrium mole fractions of components 1 and 2, respectively, in the liquid phase. The surface concentration in the liquid-vapour interface corresponds to the terms n_1^s and n_2^s of equation (45) and the surface excess to the term $\frac{n_0 \Delta x}{m}$. For comparison of the liquid-vapour and liquid-solid interfaces, we can write

$$-\Gamma_2^{(N)} = \Gamma_1^{(N)} = \frac{n_2 \Delta x}{S m} \quad \text{--- --- ---} \quad (46)$$

Where S is the specific surface area of the solid.

The surface concentration for each component, when surface layer is assumed to be one molecule thick, can be obtained by solving the equation (36) and the following equation[6]:

$$\frac{\Gamma_2^s}{(\Gamma_2^s)_m} + \frac{\Gamma_1^s}{(\Gamma_1^s)_m} = 1 \quad \text{--- --- ---} \quad (47)$$

where $(\Gamma_1^s)_m$ and $(\Gamma_2^s)_m$ are the number of moles of components 1 and 2, respectively, to form a complete monolayer. Γ_1^s and Γ_2^s are the total number of moles of components 1 and 2, respectively, present in the adsorbed layer per unit area of surface. The first two quantities can be calculated from the area occupied by each molecule, assuming a definite orientation at the interface.

Proposals have also been made to calculate the actual concentration of each component at the interface from $\Gamma_1^{(V)}$. Bartell and Banner[13] used the equation

$$Z_2 = \Gamma_2^{(V)} + \frac{V_2 N_2}{mV} , \quad - \; - \; - \; - \qquad (48)$$

where Z_2 is the number of molecules of solute (component 2) present in 1 sq.cm. of interface, V_2 is the molar volume of the solute, m its molar area, N_2 its mole fraction in the solution and V the molar volume of the solute. In order that Z_2 may be obtained by using this, an estimate must be made of the molecular area of the solute at the interface, but this procedure is not identical to the one based on the N convention in which molecular areas of both components is considered. In principle, when the values of $\Gamma^{(V)}$ are used it would seem desirable to estimate Z_1 and Z_2 if the results are to be as satisfactory as those based on the $\Gamma_2^{(N)}$ convention.

Although there has been some controversy concerning the thickness of the adsorbed layer at the liquid-solid interface, it seems generally to have been assumed that the adsorbed phase at the liquid-vapour interface is confined to the thickness of one molecule. This, as Guggenheim and Adam pointed out[7] is the simplest assumption to be made. The general assumption appears to be accepted mainly because it gives results compatible with the values of Γ derived from Gibbs equation.

Systems like water + methyl alcohol and water + ethanol have been studied[14] and the adsorbate has been shown to be confined to a monolayer. Here the analysis depended on the choice of suitable molecular areas for the two components, for water, 10 sq.A, and for ethanol, 18.4 sq.A, which corresponds to the orientation with the major axis of the molecule perpendicular to the surface and the -OH group pointing towards the solution. For methyl alcohol the molecular area was taken as 16.9 $\overset{2}{A}$.

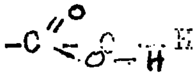
Schofield and Rideals' treatment[15] for dilute solutions is another justification for the monolayer hypothesis. They defined a quantity F ;

$$F = \gamma_0 - \gamma \qquad (49)$$

where γ_0 is the surface tension of the pure solvent and γ is that of solution, and found that a number of data fitted the equation

$$F\ (A - B) = kT\chi \qquad (50)$$

Where A is the area available to each solute molecule in the surface layer, B the minimum area which each solute molecule can occupy, k is the Boltzmann constant and $\frac{1}{\chi}$ is a measure of molecular cohesion. Application of this equation to data obtained by Szyszkowski[16] showed that n-butyric , n-valeric and n-caproic acids have the same molecular orientation with an area close to that expected for formation of a complete monolayer.

The solubility of butyric acid in (polar) water has been reported by Harkins[17] as due to the polar  $-C{\overset{O}{\diagup\!\!\diagup}}\!\!\!\!\diagdown O-H$ or carboxyl group and its solubility in (Non polar) benzene due to the non-polar $CH_3 \cdot CH_2 \cdot CH_2-$ or alkyl group. At the interface however each end of the molecule can be in that phase in which it is most soluble, that is, the carboxyl group will dissolve in water and the hydrocarbon chain in the benzene if the interface between water and benzene is considered. Thus the solubility of butyric acid should be greater at the interface than in either phase, and that this is true is indicated by the fact that this acid greatly decreases the interfacial tension in such a system.

At the interface between two pure liquids the molecules are oriented in such a way that their like parts come together in conformity with the general principle. Hence at interfaces between organic liquids and water for example the organic radical sets towards the organic liquid. If the solvent is polar, as water, then solutes will, in general, be positively adsorbed at the surface if they are less polar than water, and the least polar end of the molecules will be turned away from the water. Solutes more polar than water are negatively adsorbed.

The variation of the surface tensions of relatively concentrated aqueous solutions of soluble fatty acids with concentration can be represented by an equation of the form proposed by B. Szyszkowski[18]

$$\frac{\gamma}{\gamma_0} = 1 - X \ln \frac{c}{\gamma} \quad . \quad - \quad - \quad - \quad - \qquad (51)$$

where γ and γ_0 are the surface tensions of solution of concentration c and of pure water, respectively, and X and Y are constants; X is a constant for a series of fatty acids containing from two to six carbon atoms, but Y decreases with increasing length of the hydrocarbon chain. If equation (51) is differentiated with respect to ln c, it follows that

$$\frac{d\gamma}{d\ln c} = -X\gamma_0 \quad . \; - \; - \; - \; - \qquad (52)$$

If this value of $\frac{d\gamma}{d\ln c}$ is substituted in the approximate form of the Gibbs equation, in which concentrations replace activities, it is seen that

$$\Gamma_2 = \frac{X}{RT}\gamma_0 \quad . \; - \; - \; - \qquad (53)$$

Since X is the same for a series of fatty acids and γ_0 is constant, it is evident that in the fairly concentrated solutions considered, the excess of fatty acid at the air-solution interface becomes constant and independent of the nature of the acid. Such a result is best explained by supposing that the material adsorbed at the interface forms a single layer of molecules, and that as the concentration of fatty acid in the bulk phase increases the amount adsorbed increases until a complete unimolecular layer is formed.

Orientation of the molecules at an interface is of great importance in interpretating surface excess data. Thus , if a molecule is highly unsymmetrical, the orientation which it adopts may considerably alter the number of molecules which can occupy unit area of surface and hence the magnitude of Γ_2 .

Surface Tension. The fundamental property of liquid surfaces is that they tend to contract to the smallest possible area. This tendency is shown in the spherical form of small drops of liquid, in the tension exerted by soap films as they tend to become less extended, and in many other properties of liquid surfaces. Molecules possess size and shape, and they are free to move relative to one another, in liquids they are kept close to each other by the cohesional forces between them.

In the interior of a liquid each molecule is surrounded by other molecules on every side; it is therefore, subject to attraction in all directions. At the surface, however, conditions are entirely different. The molecules at the surface are attracted inwards and sideways by their neighbours, but there is no outward attraction to balance the inward pull. Hence every surface molecule is subject to a strong inward attraction perpendicular to the surface. This inward attraction causes the surface to diminish in area because the surface molecules are continuously moving inwards more rapidly than others move outwards to take their places; the number of molecules in the surface is therefore continually diminishing and the contraction of the surface continues until the maximum possible number of molecules are in the interior, i.e. until the surface is the smallest possible for a given valume, subject to the external conditions or forces acting on the curved surface.

The fact that a liquid surface contracts spontaneously shows that there is free energy associated with it, that work must be done to extend the surface. This free energy in the surface is of fundamental importance; a vast number of problems relating to the equilibrium of surfaces can be solved without knowing more than the magnitude of this free energy. In the solution of such problems it is often possible to substitute for the surface free energy a hypothetical tension, acting in all directions parallel to the surface, equal to the free surface energy. This is what is generally known as the surface tension. Such a surface tension has, of course the same dimensions as surface energy $(\frac{\text{mass}}{\text{time}^2})$, and it must have the same numerical magnitude. The work done in extending a surface which is pulling with a tension γ dynes per cm. by one sq. cm. will be γ ergs per sq.cm. and hence the free energy of such a surface will be γ ergs per sq. cm. Surface tension is simply defined as the force in dynes acting on the surface at right angles to any line of one cm. length.

The innumerable methods[19] that have been described for the measurement of surface tension can be classified into six main groups; (a) direct measurement of capillary pull (b) capillary rise (c) bubble pressure (d) size of drops (e) shape of drops or bubbles (f) dynamic methods. The differential capillary rise method is one of the most conve-

-nient and quite accurate absolute methods and is the one used in this work.

The elementary theory of capillary rise equates the upward pull of surface tension, $2\pi r\gamma$ (r is internal radius of the capillary tube and γ = surface tension) with the weight of column of liquid, $\pi r h d g$, where d is the density of liquid. Hence for two tubes

$$r_1 h_1 = r_2 h_2 \qquad - \quad - \quad - \quad - \qquad (54)$$

and the difference of level, Δh (= $h_1 - h_2$), is given by:

$$\Delta h = \frac{\gamma}{d}\left[\frac{2}{g}\left(\frac{1}{r_1}-\frac{1}{r_2}\right)\right]. \qquad - \quad - \quad - \qquad (55)$$

For greater accuracy the Poisson-Rayleigh formula can be used to allow for the weight of liquid contained in the meniscus. This correction is equivalent to the addition of a small height to the capillary rise, h. The effective height H is given by

$$H = \frac{2\gamma}{rdg} = h + \frac{r}{3} - 0.1288\,\frac{r^2}{h} + 0.1312\,\frac{r^3}{h^2}. \qquad - \quad - \quad - \qquad (56)$$

For tubes having r smaller than 0.2 mm. the last two terms are quite negligible, and even for tubes up to r = 1mm. the last term can be neglected if an accuracy of 0.1% is sufficient.

When these corrections are applied to the differential apparatus, the two capillary rises are given by

$$H_1 = \frac{2\gamma}{r_1 d g} = h_1 + \frac{r_1}{3} - 0.129 \frac{r_1^2}{h_1} \quad . \quad - \; - \; - \; - \qquad (57)$$

$$H_2 = \frac{2\gamma}{r_2 d g} = h_2 + \frac{r_2}{3} - 0.129 \frac{r_2^2}{h_2} \quad . \quad - \; - \; - \; - \qquad (58)$$

The differential height Δh is therefore given by the equation

$$\Delta h = \frac{2\gamma}{dg}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) + \frac{1}{3}\left(r_2 - r_1\right) - 0.129 \frac{r_2^2}{h_2} \quad . \qquad (59)$$

<u>Activity.</u> The departure from ideal behaviour of a solution may be represented in terms of a property known as activity. The concept of activity is equally applicable to solutions of electrolytes and non-electrolytes. The total free energy change for the transfer of one mole of solvent from one solution to another solution (of the same solvent and solute but of different concentration) is given by the equation[8]

$$\Delta F = RT \; \mathrm{In} \; \frac{p''}{p'} \quad . \quad - \; - \; - \qquad (60)$$

Where p' is the vapour pressure for one solution at which the solution and its vapours are in equilibrium, p" is the vapour pressure for a second solution at which it is in equilibrium with its vapours.

If F' represents the actual free energy of one mole of solvent in one solution and F'' the value in the other solution, then since the latter solution gains one mole while the former loses one mole, the free energy increase ΔF is equal to $F''-F'$ and (60) can be written as

$$F'' - F' = RT \ln \frac{p''}{p'} \qquad (61)$$

If both solutions behave ideally, the vapour pressure will be proportional to the mole fraction of the solvent in the particular solution, and hence for ideal solution, equation (61) becomes

$$F'' - F' = RT \ln \frac{x''}{x'} , \qquad (62)$$

where x', x'' are mole fractions of the solvent in the two solutions.

For non-ideal solutions this result is not applicable but the activity of the solvent, represented by a, is defined in such a way that the free energy of transfer of one mole of solvent from one solution to the other is given by

$$F'' - F' = RT \ln \frac{a''}{a'} \qquad (63)$$

This means that the activity is a property for real solutions that takes the place of the mole fraction for an ideal solution, in the free energy equation. Equation (63) does not define the actual or absolute activity but rather the ratio of activities of the particular substances in two solutions. In order to be able to express activities numerically, it is convenient to choose for each constituent of the solution a reference state or standard state in which the activity is arbitrarily taken as unity and equation (63) becomes

$$F'' - F' = RT \ln a. \qquad (64)$$

If the molar concentration or molarity of the solute is c moles per litre, it is possible to express the activity a by the relationship

$$a = f\,c \quad \text{or} \quad f = \frac{a}{c}, \qquad (65)$$

where f is known as activity coefficient of the solute. Upon inserting this into equation (64) we get the expression

$$F'' - F' = RT \ln fc, \qquad (66)$$

which is applicable to ideal and non-ideal solutions.

Several methods have been devised for the determination of activities. In the present work these are evaluated from vapour pressure data. The comparison of equation (66) with (63) shows that the activity of the solvent in a solution must be proportional to the vapour pressure of the solvent over the given solution. So $a = \frac{p}{p^\circ}$ where p is the vapour pressure of solution and p° is of pure solvent at a given temperature; but this relation gives and approximate values of activity.

Martire, Pecsok and Purnell have used the following relation for calculating the activity coefficients of some solvents at different mole fractions and here a similar relation was used for calculating the activities of the solvents[2].

$$\ln f_1 = \mathrm{In}\left(\frac{p_1}{x_1 p_1^\circ}\right) - \left[\frac{(B_{11} - V_1^\circ)(p_1^\circ - p_T)}{RT}\right] \quad \text{(67)}$$

Where f_1 = Activity coefficient of solvent.

p_1 = Partial vapour pressure for solvent.

x_1 = Mole fraction of solvent in the liquid phase.

p_1° = Vapour pressure of pure solvent.

V_1° = Molar volume of solvent at temp. $T^{\circ\circ}$K.

p_T = Total vapour pressure of the system.

T = Temperature in $^{\circ}$K.

R = Gas constant.

B_{11} = Second virial coefficientof solvent.

Using this method one can calculate the coefficients of activity for the solvents but a more convenient procedure for a not so volatile component, e.g. the solute is to calculate the activity using another method, but making use of the activity of the solvent obtained from vapour pressure data. Thus the chemical potential of any component i in a liquid solution is given by

$$\mu_i = \mu^0 + RT \ln p_i \quad , \quad - - - - - \qquad (68)$$

where p_i is the vapour pressure of the component in the vapour in equilibrium with the solution, μ^0 is a constant at a fixed temperature and pressure. For non-ideal solutions p_i in the above equation must be replaced by a_i the activity of the component, i.

Since the chemical potential is a partial molal quantity, it follows that on combining (68) with a form of Gibbs-Duhem relation $n_1 \cdot d\mu_1 + n_2 d\mu_2 = 0$ – – (69)

we have $n_1 d\ln a_1 + n_2 d\ln a_2 = 0$, – – (70)

where n_1 & n_2 are numbers of moles of solvent and solute respectively. But for a solution, $x_1 + x_2 = 1$

or $$dx_1 + dx_2 = 0 \quad \text{so that} \qquad (71)$$

$$x_1 \frac{dx_1}{x_1} + x_2 \frac{dx_2}{x_2} = 0 \;, - - - - \qquad (72)$$

where x denotes mole fraction . Hence

$$x_1\, d\ln x_1 + x_2\, d\ln x_2 = 0 . - - - - \qquad (73)$$

Subtracting (73) from (70)

$$n_1\, d\ln \frac{a_1}{x_1} + n_2\, d\ln \frac{a_2}{x_2} = 0 . - - - - \qquad (74)$$

On re-arranging and integrating equation (74) between n_1 and infinite dilution we have

$$\ln \frac{a_2}{x_2} = - \int_{\infty}^{n_1} \frac{n_1}{n_2}\, d\ln \frac{a_1}{x_1} \quad - - - \qquad (75)$$

or $$\ln f_2 = - \int_{\infty}^{n_1} \frac{n_1}{n_2}\, d\ln f_1 . \quad - - - \qquad (76)$$

In the present work the activities of solutes were calculated by using the equation (76) . The area under the curve of $\frac{n_1}{n_2}$ against $\ln f_1$ between the limits $\frac{n_1}{n_2} = \infty$ and that corresponding to a given concentration gives the value of Inf$_2$.

CHAPTER 3

Surface Excess at the Liquid-Vapour Interface: Historical Developments.

It is a well-known principle in thermodynamics, that any process tends to occur spontaneously, if it is accompanied by a decrease in free energy. If therefore the addition of butyric acid to water lowers the surface tension or free surface energy, it is to be expected that the acid will spontaneously diffuse into the interior region from the body of the liquid in order to bring about as great a reduction in free energy as possible. In general, a concentration of any component in the interface region should be smaller or greater than in the adjacent phases according as an increase in concentration of the component increases or decreases the free interfacial energy. These two possibilities can be referred to as negative and positive adsorption respectively. This thermodynamic consequence was first recognised and quantitatively formulated by J.W.Gibbs in 1876 in the form of the differential equation

$$\partial\gamma = \Gamma_1 \partial\mu_1 - \Gamma_2 \partial\mu_2 - - - - \Gamma_n \partial\mu_n, - - - \quad (77)$$

where γ is the free interfacial energy, $\mu_1, \mu_2 \ldots \mu_n$ are the chemical potentials of various components in the phases on both sides of the interface. While $\Gamma_1, \Gamma_2, -- \Gamma_n$ are the number of grams of these components that must be added to the system to maintain the corresponding potentials constant when the interface is increased by 1cm^2, temperature, pressure, and any other variables being constant. For two component systems the following equation was reported by Gibbs which has been of great help to different workers:

$$\Gamma_2 = - \frac{1}{RT} \frac{d\gamma}{d\ln a_2}, - - - \quad (39)$$

where Γ_2 is the excess surface concentration of solute, as already defined.

Harkins and Wampler[4] determined the activity values for solutions of n-butyl alcohol and water by the use of a specially designed apparatus for the determination of the lowering of the freezing point[4]. They used the following Gibbs equation for the calculation of the adsorption: $u = \frac{1}{RT} \cdot \frac{d\gamma}{d\ln a}$, - - - - (78)

where the value of adsorption (u) gives the number of moles of solute which must be added to the whole sulution in order to keep the activity of the solute constant when the area of the surface of the solution is increased by one sq. cm. They concluded that the film of alcohol on its aqueous solutions was monomolecular and that the area per molecule of alcohol in the film was 23.7Å^2. To obtain the total number of moles of solute Γ_2^{s} in the surface layer, they added to the surface excess the number of moles of solute which would be present in unit area of surface if $\Gamma_2^{(1)}$ were zero. This latter term was estimated, for 1cm^2. of surface, as the two-thirds power of the number of moles present in 1 ml. of solution.

Butler[20] did not agree with the assumptions of Harkins and Wampler. He pointed out that the number of moles of solvent in unit area of surface can be calculated from the following equation:

$$\Gamma_2^{s} = \Gamma_2^{(1)} + \frac{x_2}{x_1}\Gamma_1^{s}, \quad - - - (79)$$

where x_2 and x_1 are the respective mole fractions of the solute and the solvent in the bulk phase. Γ_2^s is the number of moles of solute per unit area of surface.

Butler and Wightman have discussed the thickness of the adsorbed layer of ethyl alcohol + water system.[21] They gave the following relations between the Gibbs adsorption (surface excess) and the total number of molecules present at the surface: $A_1\nu_1 + A_2\nu_2 = 1$ --- (80)

$$\Gamma_2 = \frac{1}{A_2} - \left(\frac{A_1}{A_2} - \frac{N_2}{N_1}\right)\nu \text{ , } \quad ---- \quad (81)$$

where N_1 and N_2 are the molar fractions in the bulk of the solution of the two components, A_1 and A_2 are the superficial areas of the two components, $\frac{1}{A_2}$ is the maximum number of molecules of component 2 which can be present in unit area, ν_1 and ν_2 represent the number of molecules of components 1 and 2 respectively per sq.cm. of the surface layer. They concluded that the observed adsorptions are inconsistent with the hypothesis that only a single layer of molecules at the surface differs in composition from the bulk of the solution.

Guggenheim and Adam in discussing the thermodynamics of adsorption at the surface of solutions[7], stated that the Gibbs adsorption equation was deduced with the aid of a particular choice of the position of a mathematical surface, such that the surface excess of one of the components varied. They examined the form taken by the General Gibbs equation when other conventions relating to the position of the dividing surface were chosen. The quantitative relations between the values of the surface excess of each component, obtained by the use of various conventions were thus established. They took the water + ethyl alcohol system as an example and calculated the surface excess according to convention N.

Belton[5] calculated the adsorption at the surface of some binary liquid mixtures with the help of surface tension and activity data. In the case of the system benzene + acetic acid he reported that the adsorption of benzene increased with increasing benzene concentration in the liquid phase, reached a miximum and then fell to zero after which acid was adsorbed preferentially. But in the case of the system benzene + carbon disulphide he reported that benzene was preferentially adsorbed throughout, and a maximum was rapidly attained after which the adsorption fell to very low value. In the benzene + carbon tetrachloride system the latter component was adsorbed, at first in increasing amount with increasing carbon tetrachloride content; no maximum was however observed and ~~but~~ the adsorption tended to a steady value.

Schay, Nagy and Szekrenyesy studied the adsorption equilibrium of liquid mixtures on solid/liquid and liquid/gas interfaces[22]. The systems chosen were AcOH + C_6H_6 and AcOH + C_6H_6 + charcoal. The adsorption at the liquid - vapour interface by surface tension determinations by the drop-weight method, and the adsorption on the solid surfaces was determined by concentration changes occurring in the liquid phase. Going from one type of interface to the other they noted a reversal in the surface excess values and postulated that for such a reversal to occur the free energies of the pure components must be small and the mixtures must deviate from ideal behaviour.

Cornford, Kipling and Wright[23] have applied a method of an analysis to some systems in estimating the thickness of the adsorbed phase at the liquid-solid and liquid-vapour interfaces. They considered the data calculated by Guggenheim and Adam for ethyl alcohol + water mixtures at 25° and have suggested that the adsorption was confined to approximately one molecular layer, in contrast to earlier suggestions that it was more complex.[21]

Kipling has made much contribution in the field of adsorption. Although much of his work has been on solid-liquid interface yet his work on the other interfaces is of considerable importance.[6] He examined the surface composition of aqueous solutions of some alcohols. For surface excess he preferred the use of the convention denoted as Γ_2^{N} which is the number of moles of component 2 in unit area of the surface in excess of the number present in that part of the bulk phase which contains the same total number of moles of solute plus solvent. From Γ_2^{N} values he calculated Γ_1^{s} and Γ_2^{s} (the total number of moles of solute and solvent respectively present in unit area of the surface) by the use of the following equations:

$$\Gamma_2^{n} = \Gamma_2^{s} x_1 - \Gamma_1^{s} x_2 \quad - - - - \qquad (36)$$

$$\frac{\Gamma_2^{s}}{(\Gamma_2)_m} + \frac{\Gamma_1^{s}}{(\Gamma_1)_m} = 1 \; . \quad - - - - - \qquad (47)$$

He reported that the values of Γ_2^{s} calculated from Γ_2^{n} for butyle alcohol and water system agreed closely with those calculated on slightly a more approximate basis from $\Gamma_2^{(1)}$.

The individual isotherms for different systems were presented and he reported that the complete monolayer of alcohol was formed only from the pure components. The isotherms were similar for the first three alcohols and for the higher alcohols, such as n-amyl alcohol and n-hexyl alcohol, the curves were similar to that of butyl alcohol.

Kipling concluded that the surface layer did not tend to form a complete monolayer of butyl alcohol molecules but approximated to a 1/1 ratio of alcohol and water molecules at the higher relative concentration. This result was contrary to the one put forward by Harkins and Wampler[4], who concluded that the surface layer tended to a complete monolayer of butyl alcohol (the molecules being oriented with the major axis parallel to the surface) as the concentrations tended to the miscibility limit. The molecular area used was 10 sq. A for water and 18.4 sq. A for the alcohols with the exception of methyl alcohol for which a value of 16 sq. A was used.

Trapeznikov and Ogarev [24] have studied monolayers of higher secondary alcohols (C_{15} to C_{26}) at water-air interface at 20°. They concluded that all alcohols formed liquid expanded monolayers except $CH_3(CH_2)_{17}CHOH \cdot CH_3$ which formed a condensed layer.

Rusanov and Levichev has applied the concept of "finite thickness layer" to derive equations for the calculation of surface tension isotherms and composition of surface layers from the data on vapour-liquid equilibrium. They found that in the hexane + ethyl alcohol and hexane + acetone systems the concept of a unimolecular surface layer was invalid over a certain bulk concentration range.[25]

Rusanov, Levichev and Tyushin studied the composition of the surface layer in the binary system n-hexane + acetone.[26] The surface tension measurements were done by the maximum bubble pressure method, and vapour pressure data were obtained at 25°. The regular composite isotherm, which was in agreement with the conditions of thermodynamic stability, was obtained when a di - or tri-molecular layer was considered. They also reported that the thickness of the layer increased with temperature.

Martire, Pecsok and Purnell measured the surface tension and activity coefficients of highly dilute solutions of a volatile solute in a involatile solvent.[2] The date which were for the region of zero concentration were used in the Gibbs adsorption isotherm to compute surface excesses at the liquid-vapour interface. The general equation derived for the monolayer mole fraction of the solute is given below:

$$\theta_2 = \frac{\bar{A}_1 x_1 \Gamma_2^{(1)} + x_2}{x_1 \Gamma_2^{(1)} (\bar{A}_1 - \bar{A}_2) + 1} \quad . \quad - \; - \; - \qquad (82)$$

Where $\bar{A}_1$ and $\bar{A}_2$ are the areas per mole of the constituents and θ_2 represents the monolayer mole fraction of the solute.

Aveyard has measured the surface tension at 20°C for binary n-alkane mixtures (6+16, 7+16, 8+16, 10+16, 6+14, 10+14 and 6+12)where the numbers refer to the numbers of carbon atoms in the chain). He tested the applicability of some surface tension equations to these data and found a good agreement between experiment and theory on the assumption that the alkanes lie flat at the surface. He calculated the adsorption for the above systems at the solution/vapour, solution/water and solution/Graphon interfaces, at 20°C. and tested the Gibbs equation on the assumption that the adsorbed layer was one molecule thick and that the alkane molecules on average lie flat at the liquid/vapour interface.[27]

The surface excess plots for octane + hexadecane mixtures at the three interfaces showed that octane was preferentially adsorbed at the solution-vapour interface; at the solution-water interface it was still preferentially adsorbed although to a much smaller extent. At the solution-Graphon surface, however, hexadecane was reported to be strongly adsorbed.

Present Work. The work in this thesis is concerned with a systematic study of the behaviour of three monocarboxylic acids at the solution-vapour interface at 30°C. With this aim in view the surface tension and the vapour pressure (total as well as partial) of fourteen systems have been experimentally determined at various concentrations.

The surface excess Γ_2^N and the amounts of the individual components at the interface have been calculated from the surface tension and activity data. The systems chosen consisted of three solutes (acetic acid, propionic acid and butyric acid) and five solvents (benzene, carbon tetrachloride, cyclohexane, ethyl alcohol and water). The surface excess has been calculated by the use of Gibbs equation (39) in which convention N is involved. $d\gamma$ and $d\ln a_2$ were determined from graphs drawn for surface tension vs ln a_2.

The individual amounts of the components were calculated with the use of equation (36) and (47). The use of equation (47) implies, of course, that the adsorbed layer is confined essentially to a uni-molecular layer. This is the simplest assumption to make, but if such an assumption were not valid for a particular system, this would show up in the individual isotherms so calculated. It should be pointed out, however, that models involving a multimolecular adsorbed layer may also be consistent with the surface excess obtained for the systems.

The adsorption isotherms have been drawn for all the systems. The behaviour of each acid at the interface when mixed with different solvents and the behaviour of each solvent when mixed with the three acids, separately, are discussed.

CHAPTER 4

PURIFICATION OF THE CHEMICALS.

Acetic acid of AnalaR grade was refluxed for two hours with 2% chromium tri-oxide and then distilled. Then the theoretical amount of acetic anhydride was added to the middle fraction and the mixture was refluxed for one hour and fractionated. The fraction collected at 118°C was then crystallized to remove further impurities. The acid used had n_D = 1.3717 (cf. previous value of 1.3716).[28]

Propionic acid of 'Technical' grade was first dried over anhydrous sodium sulphate and then fractionally distilled. The middle fraction was collected in the range 139–141°C and refractionated over potassium permanganate. The fraction collected at 140.5° had n_D = 1.3864 (cf. previous value of 1.3865).[29]

n-Butyric acid was fractionally distilled and the fraction collected at 163°C had n_D = 1.3981 (cf. previous value of 1.39796).[30]

Benzene of AnalaR grade was dried over phosphoric oxide and fractionally distilled. The fraction collected at 80°C was further purified by fractional crystallisation. The purified benzene had n_D^{20} = 1.5010 (cf. previous value of 1.5011).[31]

Carbon tetrachloride of AnalaR grade was fractionally distilled over phosphoric oxide and the fraction collected at 76.8° had n_D^{20} = 1.4602 (cf. previous value of 1,4604[32] and 1.4603).[33]

Ethyl alcohol of AnalaR grade was purified by dissolving some sodium in it and then refluxing it after the addition of ethyl succinate (about 25 gms./lit.). It was then fractionally distilled and the fraction collected at 78°C had n_D^{20} = 1.3613 (cf. previous value of 1.3614).[30]

The sample of water used was redistilled laboratory distilled water with refractive index n_D^{20} = 1.3330 (cf. previous value of 1.3330).[34]

Cyclohexane of 'technical' grade supplied by the B.D.H. was dried over P_2O_5 and fractionally distilled. It was then fractionally crystallized. The refractive index of cyclohexane used had $n_D^{20} = 1.4263$ (cf. previous value of 1.4262).[35]

CHAPTER 5

MEASUREMENT OF SURFACE TENSION.

Surface tension was measured by the capillary rise method which is considered to be a most accurate absolute method. Volatility of some of the solvents was another factor which supported the use of this method during the present work. The following two difficulties were avoided by the use of two capillary tubes of difference diameters.

1. The necessity of having a very wide surface of liquid for the lower level if it is to be measured plane, and the consequent need for much liquid.
2. The associated experimental difficulty of accurately measuring the level of a wide surface of liquid.

A standard all-glass differential capillary rise apparatus was used. Two capillary tubes of the apparatus used had internal diameters of 0.156 cm. and 0.065 cm. respectively.

The apparatus was thoroughly cleaned with chromic acid, then with water, and finally with benzene. It was dried in an oven at 100°C. A sufficient amount of the solution, whose surface tension was to be measured, was poured into the reservoir bulb of the apparatus, and the solution was sucked up and pushed down several times by means of suction rubber bulbs to wet the inside of the capillary tubes. The apparatus was then placed in a thermostat at 30°C, (Plate A), and allowed to attain equilibrium. The heights of the liquid levels in the capillary tubes were measured by means of a cathetometer. The procedure was repeated for thesame solution as a check. The difference between the levels of liquids in both the capillary tubes was then used in the equation (59) for the calculation of surface tension. The density of the solution was measured before the measurement of surface tension; for this a dried and weighed density bottle was used. The apparatus was again cleaned with chromic acid and then with water and lastly with benzene and dried, and the procedure repeated for other concentrations of the solution.

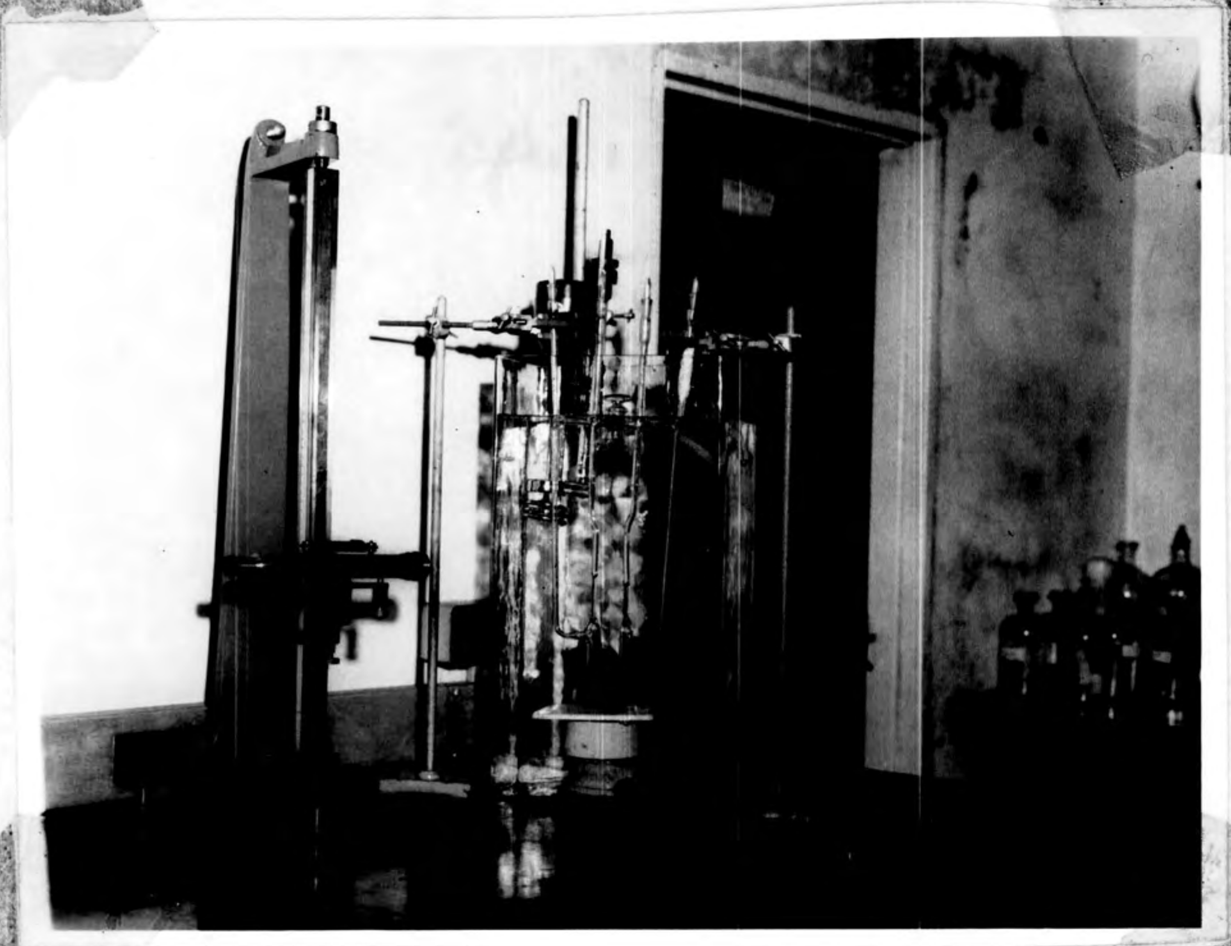


PLATE A.

CHAPTER 6

MEASUREMENT OF VAPOUR PRESSURE.

Half of the present experimental work consists of the measurement of total and partial vapour pressures of various systems for various concentrations at 30°C. Thus the method put forward by Rosanoff and his collaborators was adopted for the measurement of vapour pressures.[36]

The apparatus, figure 1, consisted of a mercury manometer M and a main side tube to which the vacuum pump was connected. The temperature of this tube was kept just above 30°C by the use of an electrically controlled air thermostat. The bigger bulb A containing the original solution was connected to the side tube through E. The contents of bulb A were stirred by the use of a magnetic stirrer. The small bulb B was connected to the main side tube through D. The working of the manometer was controlled by the use of glass stoppers F, G and H. The bulb K serves the purpose of a vapour trap.

<u>Procedure.</u> About 40 c.c. of the mixture was transferred to the

bigger bulb A, and the solution was solidified with the liquid oxygen in a flask. The system was evacuated by opening the tap E and then the solution was allowed to melt (after closing E) to remove air from the solution. Each solution was solidified, evacuated to 10^{-2} mm. and melted four to five times until completely free of dissolved air.

During these evacuations F was kept closed. Finally tap E is closed, F, G and H opened, and the whole system thoroughly evacuated.

The solution, after the final evacuation, was stirred and heated at a constant temperature of 30°C. Then taps C and G are closed and tap E opened. The solution-vapour system was allowed to come to equilibrium in the whole apparatus, with tap G closed and taps F and H opened. The difference of height of the mercury column was taken as the vapour pressure. The solution with vapour was frozen in applying a colant around bulb A, and the procedure repeated three to four times until the vapour pressure was constant.

The second stage of the experiment was to determine the concentration of vapour in equilibrium with the solution

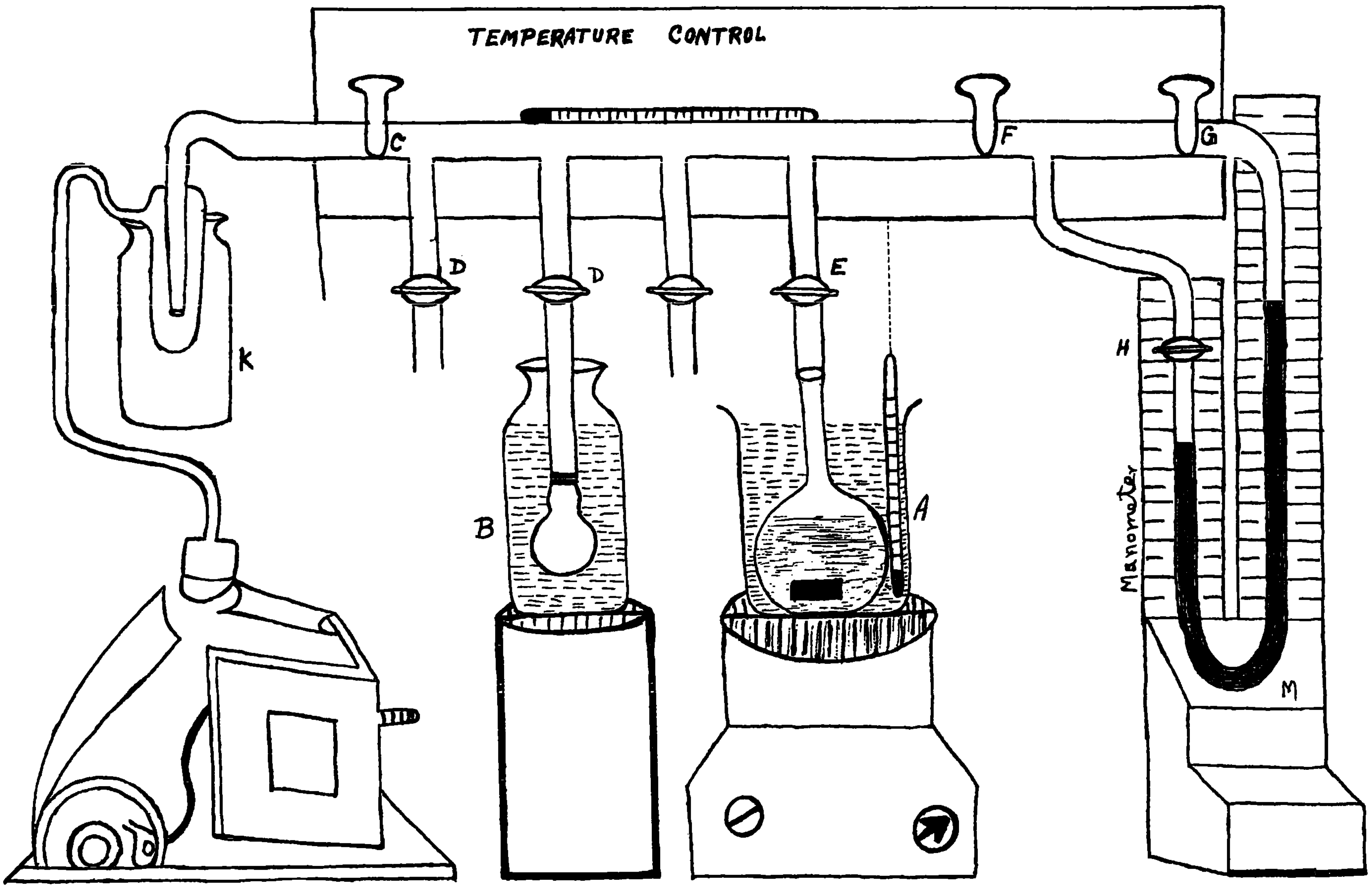


FIG. 1 – APPARATUS FOR THE MEASUREMENT OF VAPOUR-PRESSURE

in bulb A at 30°C in order to be able to calculate the partial pressures. This was done by distilling fractions into the small evacuated bulbs at B which were always kept cold by the use of liquid oxygen. In this way from 5 to 10 cc. of each distilled fraction was collected in each of the four small bulbs.

At the end of the experiment the total vapour pressure of the solution left in A was again measured at the same temperature. After this the four small bulbs were weighed and the concentrations of the five individual fractions were determined by measuring their refractive indices and comparing them with a refractive index-composition curve for the particular system. Extrapolation to zero weight of fraction distilled over gave the composition of vapour in equilibrium with solution in bulb A.

CHAPTER 7

RESULTS.

In this chapter all the results, observed as well as calculated, have been reported. The main results include the following:-

1- Vapour-pressures of all the systems;

2- Activity coefficients of the components; 1;

3- Activity coefficients of the components, 2;

4- Surface tensions and surface excesses;

5- Monolayer values and Individual isotherms;

6- The fractions of the surface covered by the three acids in different systems at different concentrations of acid in the liquid phase.

TABLE I.

Vapour-Pressure of acetic acid + benzene system.

Mole fraction of acid in bulk	Total Pressure	Partial Pressure of acid	Partial Pressure of benzene.
0.0	117.5 mm	0.0mm	117.5 mm
0.13	108.0	5.0	103.5
0.26	96.0	9.5	86.4
0.44	85.0	12.0	72.0
0.46	82.0	12.5	68.0
0.70	62.0	16.5	45.0
0.89	42.0	19.0	25.0
0.93	36.0	19.5	15.0
0.99	23.0	19.8	2.5
1.00	20.0	20.0	0.0

TABLE 2.

Vapour-Pressure of acetic acid + carbon tetrachloride system.

Mole fraction of acid	Total Pressure	Partial Pressure of acid	Partial Pressure of CCl_4.
0.0	139.5 mm	0.0 mm	139.5 mm
0.15	128.0	5.0	123.0
0.26	116.0	8.5	106.0
0.30	112.0	9.0	103.0
0.46	105.0	11.5	96.0
0.53	95.0	13.5	86.0
0.64	85.0	15.5	71.0
0.67	80.0	16.4	69.5
0.99	24.0	20.5	2.0
1.00	20.0	20.0	0.0

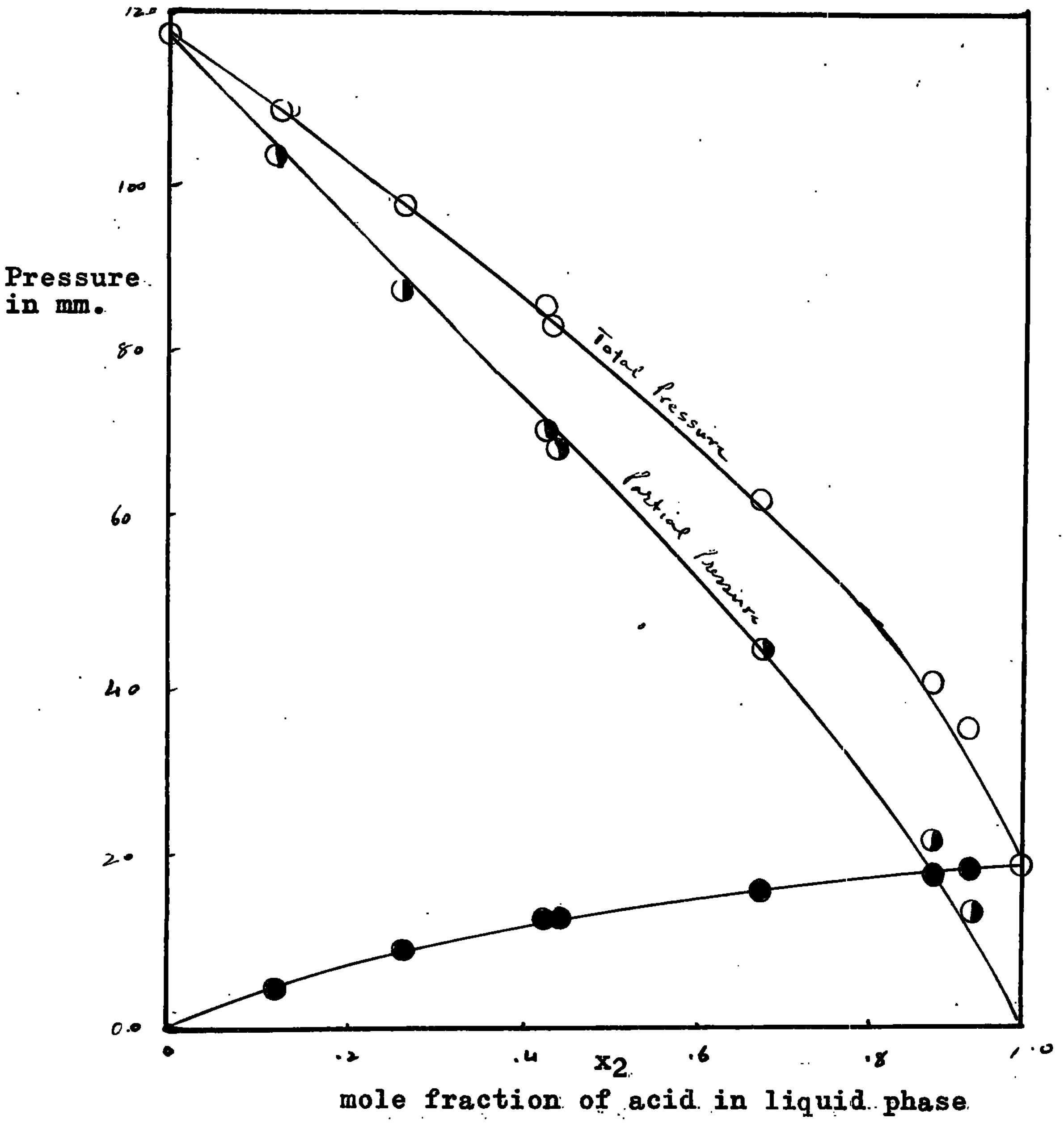


Fig.2- Vapour-pressure curves for acetic acid+benzene system at 30°C.

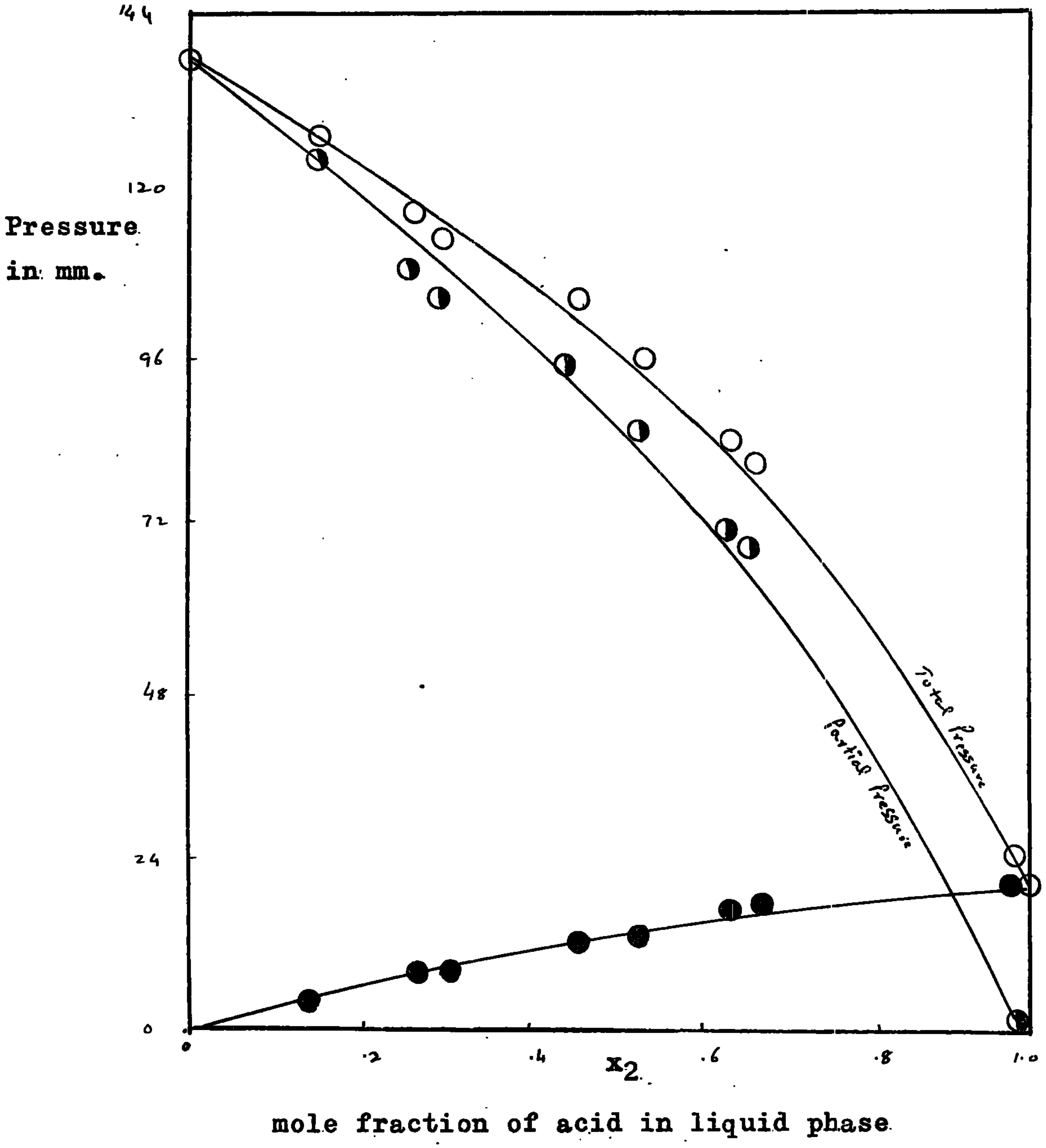


Fig.3- Vapour-pressure curves for acetic acid + carbon tetrachloride system at 30° C.

TABLE 3

Vapour-Pressure of acetic acid + cyclohexane system.

M.F. of acid in liquid phase	Total Pressure	P.P. of acid	P.P. of cycl.
0.0	121.0 mm	0.0	121.0 mm
0.26	117.0	12.0	110.0
0.38	113.0	14.0	102.0
0.49	110.0	16.0	96.0
0.62	106.0	17.5	86.0
0.83	93.0	18.5	72.0
0.95	70.0	19.0	54.0
0.99	22.0	19.0	3.0
1.00	20.0	20.0	0.0

TABLE 4.

Vapour-Pressure of acetic acid + ethyl alcohol system.

M.F. of acid	Total Pressure	P.P. of acid	P.P. of alcohol
0.0	78.0 mm	0.0 mm.	78.0 mm
0.2	66.0	3.5	61.5
0.3	60.0	5.5	54.0
0.38	56.0	6.5	48.5
0.49	49.5	9.0	40.0
0.56	45.0	10.5	33.0
0.64	40.0	13.0	28.0
0.78	30.0	15.0	17.0
0.90	25.0	18.0	7.5
1.00	20.0	20.0	0.0

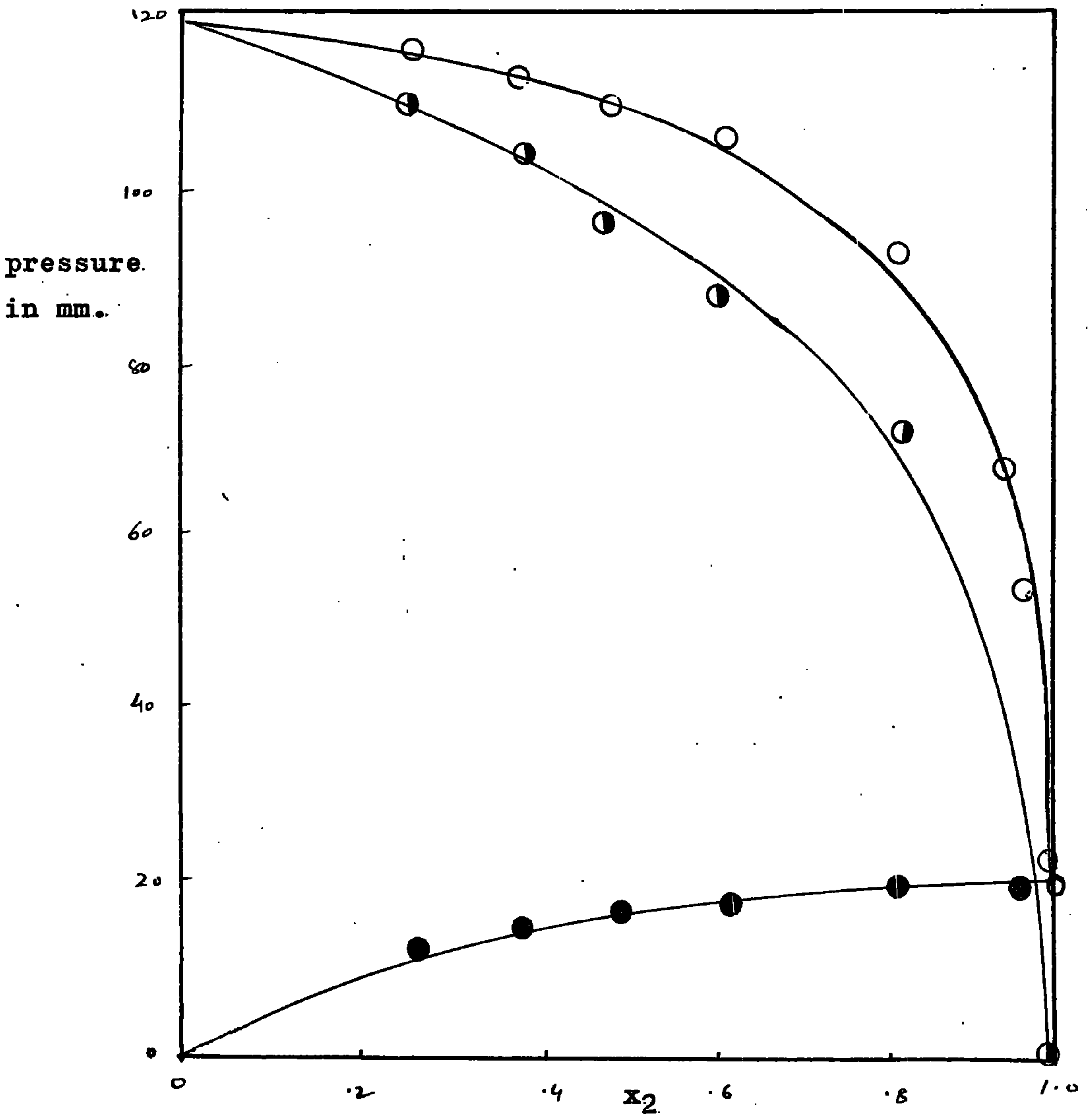


Fig.4- Vapour-pressure curves for acetic acid + cyclohexane system at 30°C.

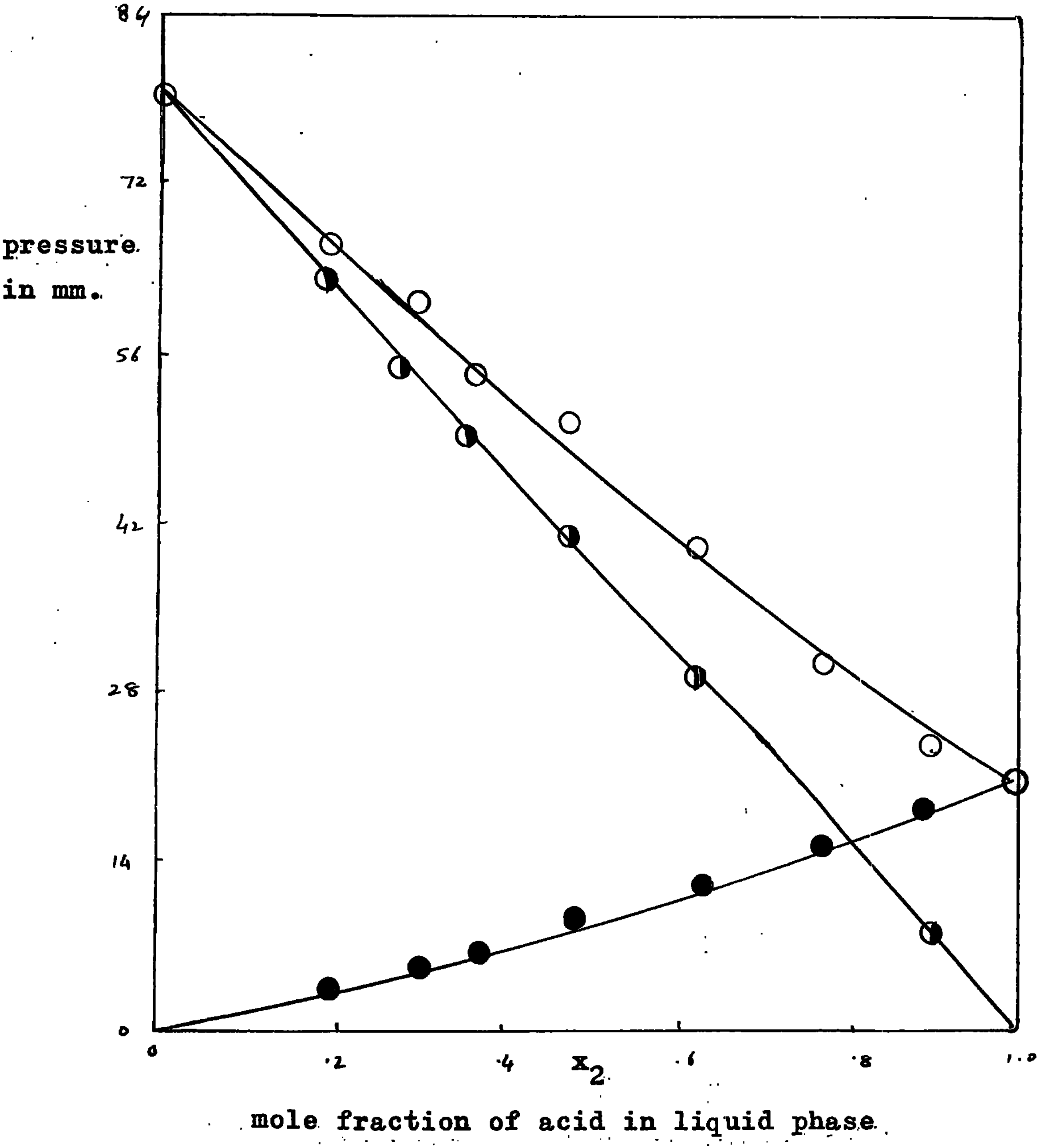


Fig.5- Vapour -pressure curves for acetic acid + ethyl alcohol system at 30° C.

TABLE 5.

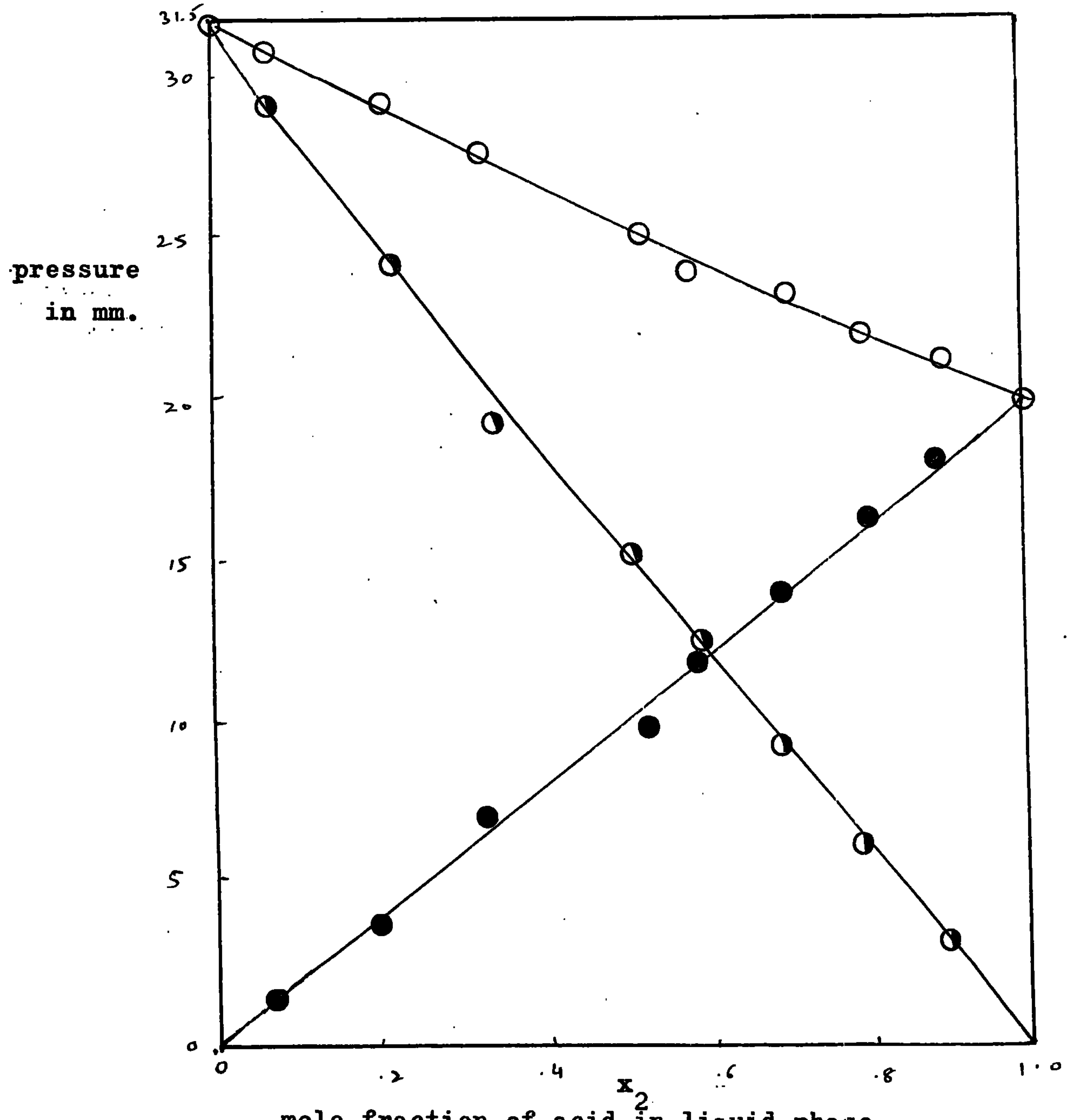
Vapour-Pressure of acetic acid + water system.

M.F. of acid	Total Pressure	P.P. of acid	P.P. of water
0.0	31.5 mm	0.0 mm	31.5 mm
0.08	31.0	1.5	29.0
0.22	29.0	4.0	24.0
0.34	28.0	7.0	19.0
0.52	25.0	10.0	15.0
0.60	23.5	12.0	12.5
0.70	23.0	14.0	9.0
0.80	22.0	16.0	6.0
0.90	21.0	18.0	3.0
1.00	20.0	20.0	0.0

TABLE 6.

Vapour-Pressure of propionic acid + benzene system.

M.F. of acid	Total Pressure	P.P. of acid	P.P. of benzene
0.0	117.5 mm	0.0 mm	117.5 mm
0.08	110.0	1.0	108.0
0.20	96.0	1.5	93.0
0.35	82.0	2.0	78.0
0.45	74.0	2.0	70.0
0.61	56.0	2.5	51.0
0.86	24.0	3.5	18.0
0.98	6.0	4.0	2.0
1.00	4.0	4.0	0.0



mole fraction of acid in liquid phase

Fig.6- Vapour-pressure curves for acetic acid + water system at 30° C.

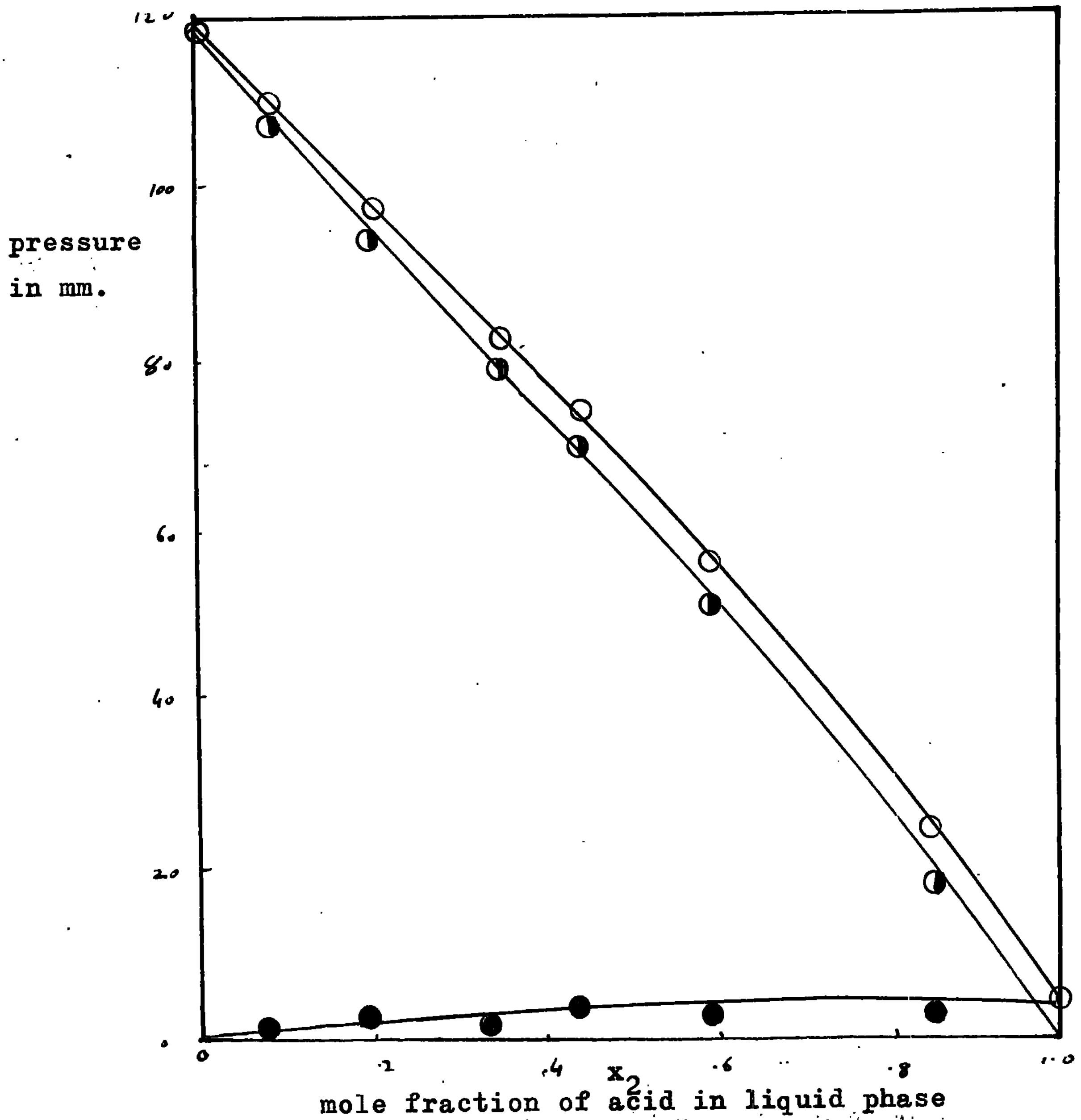


Fig.7- Vapour-pressure curves for propionim acid + benzene system at 30°C.

TABLE 7.

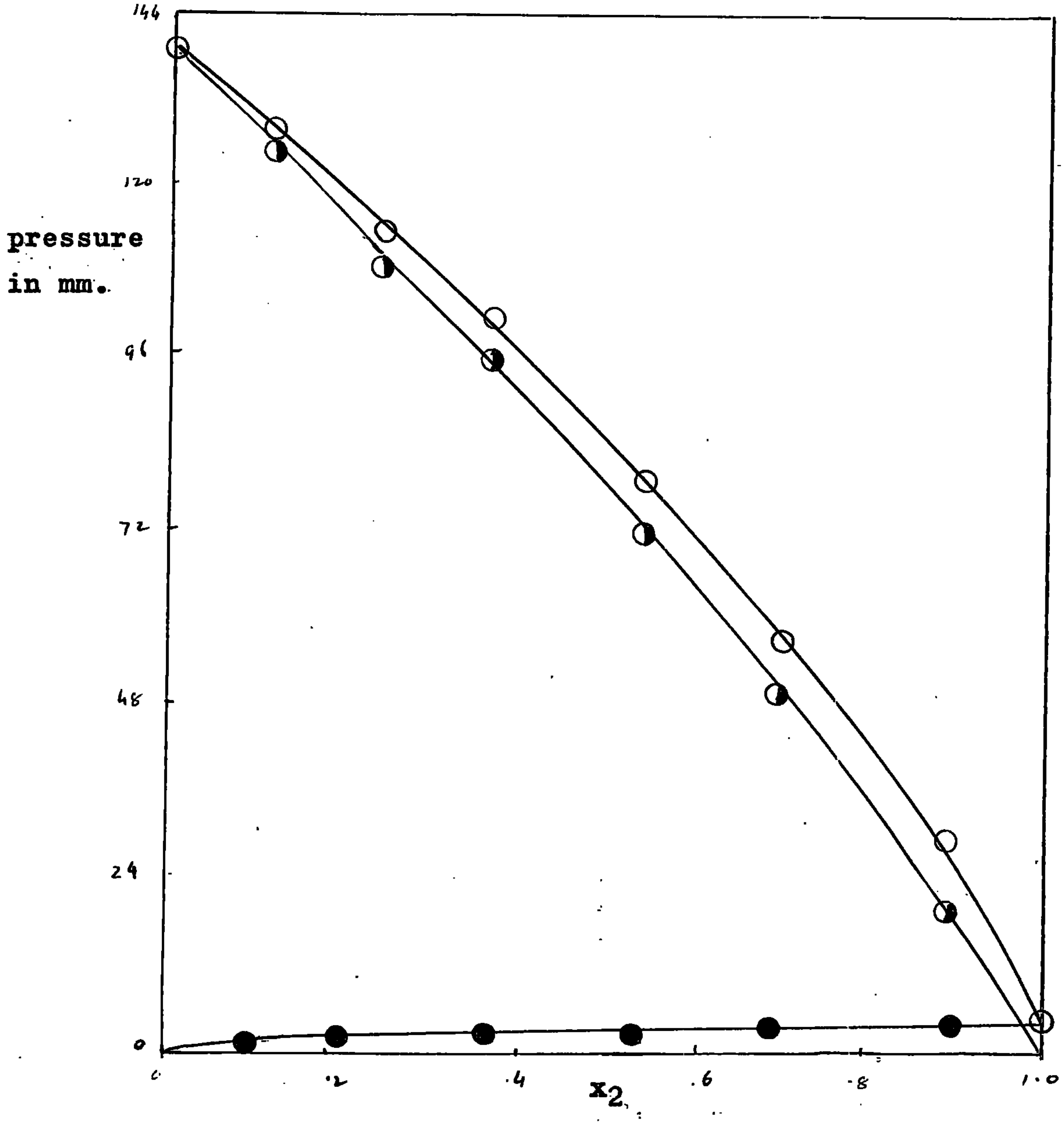
Vapour-Pressure of propionic acid + carbon tetrachloride system.

M.F. of acid	Total Pressure	P.P. of acid	P.P. of CCl_4
0.0	139.5 mm	0.0 mm	139.5 mm
0.12	127.0	1.0	123.0
0.25	112.0	1.5	107.0
0.38	95.0	1.5	89.0
0.55	78.0	2.0	72.0
0.70	58.0	2.5	51.0
0.90	30.0	2.5	24.0
1.00	4.0	4.0	0.0

TABLE 8.

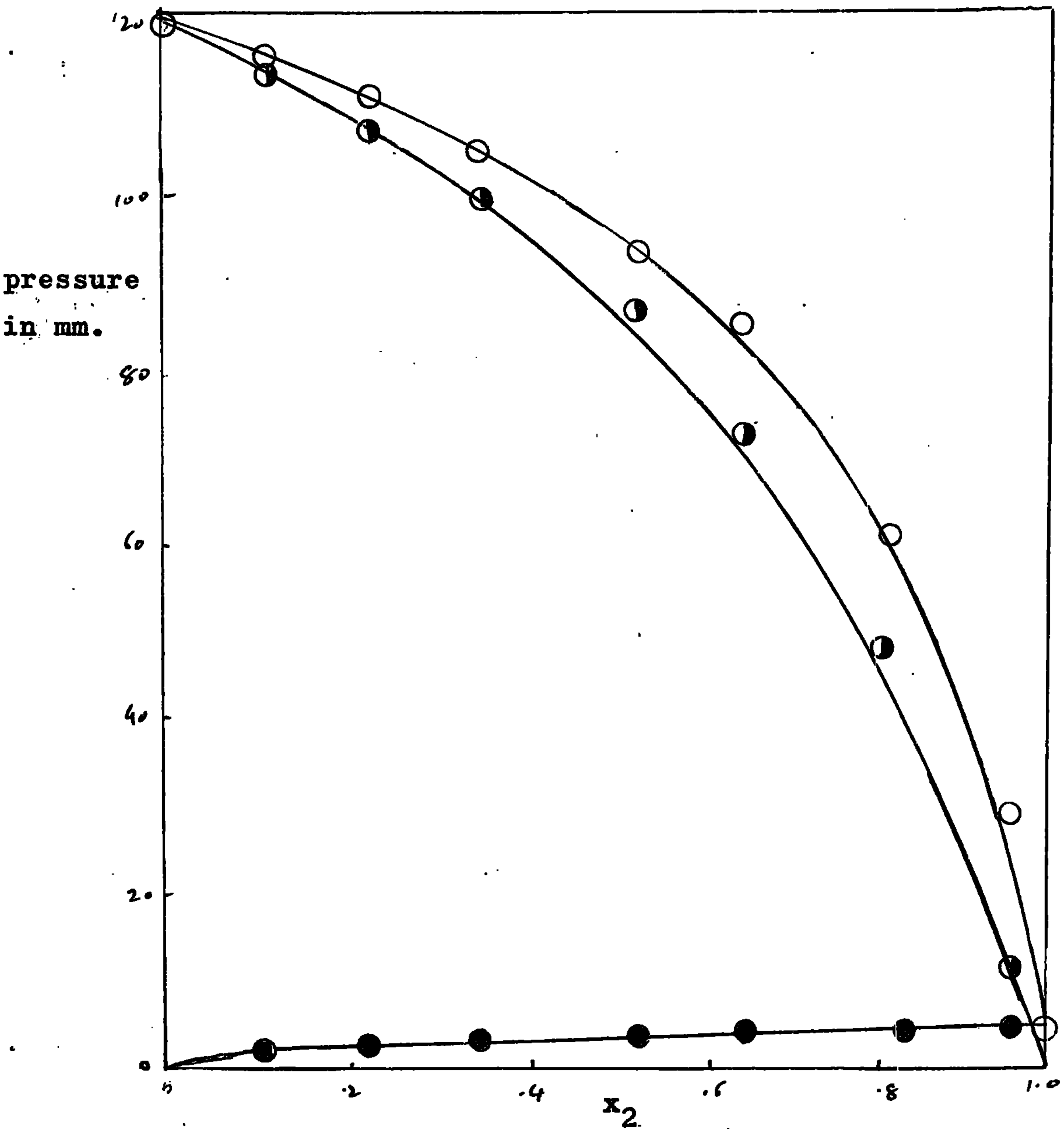
Vapour-Pressure of propionic acid + cyclohexane system.

M.F. of acid	Total Pressure	P.P. of acid	P.P. of cycl.
0.0	121.0 mm	0.0. mm	121.0 mm
0.12	115.0	1.0	113.0
0.24	112.0	2.0	108.0
0.36	106.0	3.0	101.0
0.54	93.00	3.5	87.0
0.66	84.0	3.5	72.0
0.84	60.0	4.0	40.0
0.96	28.0	4.0	10.0
1.00	4.0	4.0	0.0



mole fraction of acid in liquid phase

Fig.8–Vapour-pressure curves for propionic acid + carbon tetrachloride at 30°C.



mole fraction of acid in liquid phase

Fig.9–Vapour–pressure curves for propionic acid + cyclohexane system at 30° C.

TABLE 9.

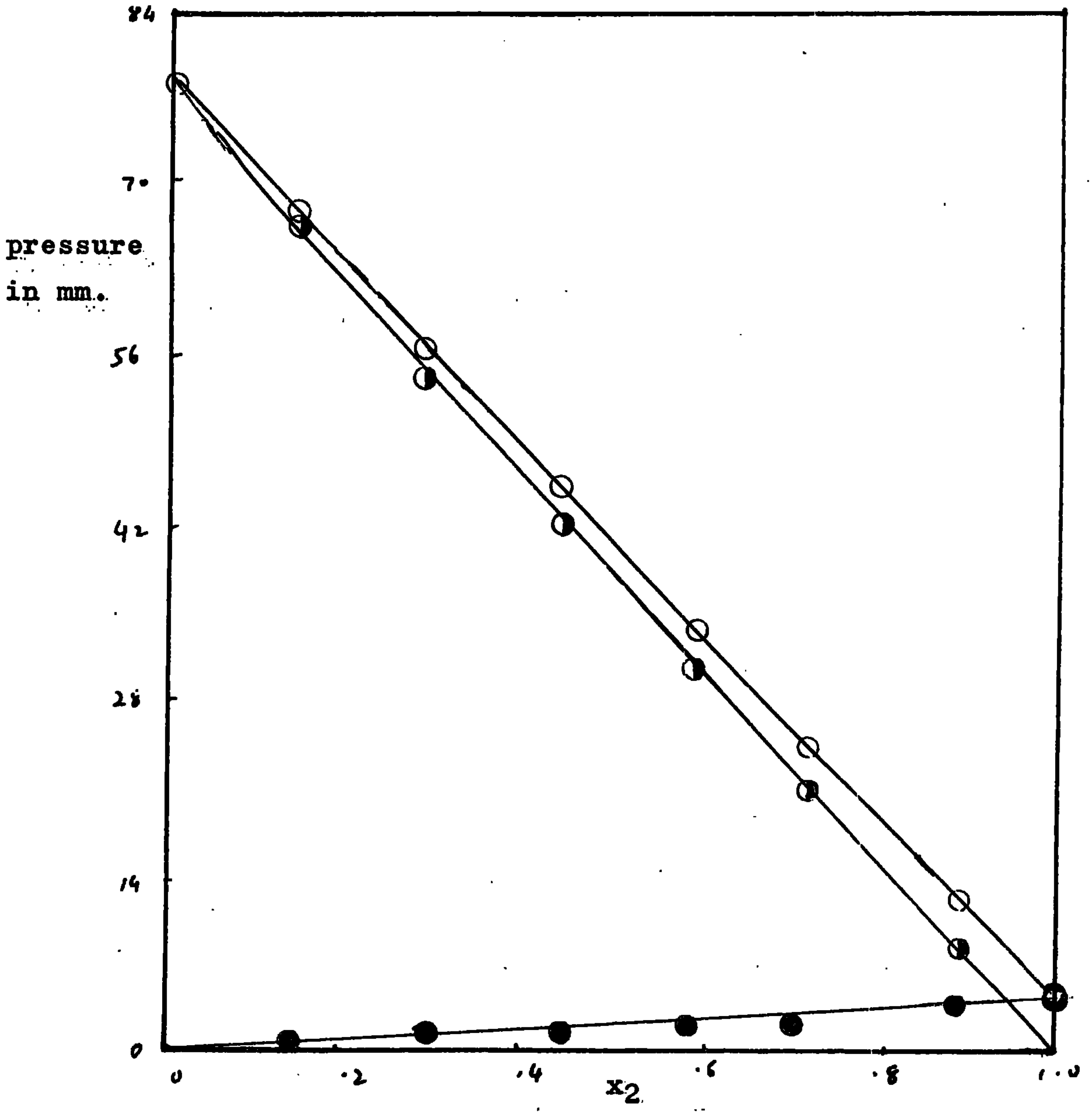
Vapour-Pressure of propionic acid + ethyl alcohol system.

M.F. of acid	Total Pressure	P.P. of acid	P.P. of ethanol
0.0	78.0 mm	0.0 mm	78.0 mm
0.15	67.5	1.5	66.5
0.30	57.0	2.0	55.5
0.45	46.0	2.5	31.0
0.72	25.0	3.0	22.0
0.90	11.0	3.5	8.0
0.96	7.0	4.0	3.0
1.00	4.0	4.0	0.0

TABLE 10.

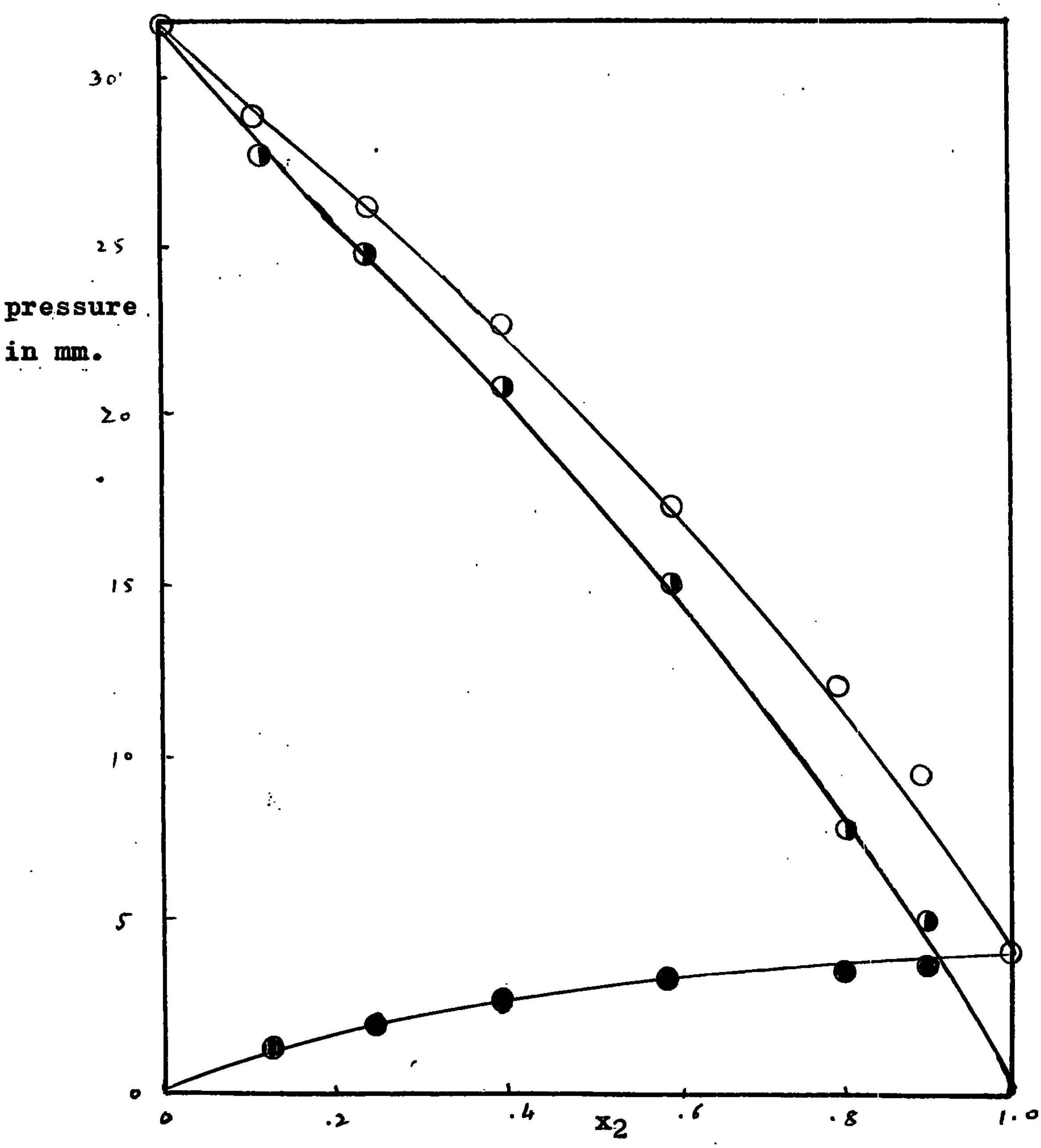
Vapour-Pressure of propionic acid + water system.

M.F. of acid	Total Pressure	P.P. of acid	P.P. of water
0.0	31.5 mm	0.0 mm	31.5 mm
0.06	30.0	1.0	29.0
0.12	28.5	1.5	27.5
0.24	26.0	2.0	24.0
0.40	23.0	2.5	21.0
0.60	17.0	3.5	15.0
0.80	12.0	3.5	7.5
0.90	9.5	4.0	5.0
1.00	4.0	4.0	0.0



mole fraction of acid in liquid phase

Fig. 10–Vapour-pressure curves for propionic acid + ethyl alcohol system at 30° C.



mole fraction of acid in liquid phase

Fig.11-Vapour-pressure curves for propionic acid + water system at 30 C.

TABLE 11.

Vapour-Pressure of butyric acid + benzene system.

M.F. of acid	Total Pressure	P.P. of acid	P.P. of benzene
0.00	117.5 mm	0.00 mm	117.5 mm
0.09	108.0	0.30	106.0
0.21	96.0	0.50	93.0
0.33	84.0	0.80	80.0
0.45	66.0	1.00	62.0
0.60	50.0	1.00	46.0
0.72	34.0	1.30	30.0
0.84	20.0	1.50	18.0
0.93	10.0	2.00	8.0
1.00	2.00	2.00	0.0

TABLE 12.

Vapour-Pressure of butyric acid + carbon tetrachloride system.

M.F. of acid	Total pressure	P.P. of acid	P.P. of CCl_4
0.00	139.5 mm	0.0 mm	139.5 mm
0.12	127.0	0.5	125.0
0.24	110.0	0.6	107.0
0.36	94.0	0.8	90.0
0.54	68.0	1.0	64.0
0.66	52.0	1.5	48.0
0.78	35.0	1.8	32.0
0.90	18.0	2.0	14.0
1.00	2.0	2.0	0.0

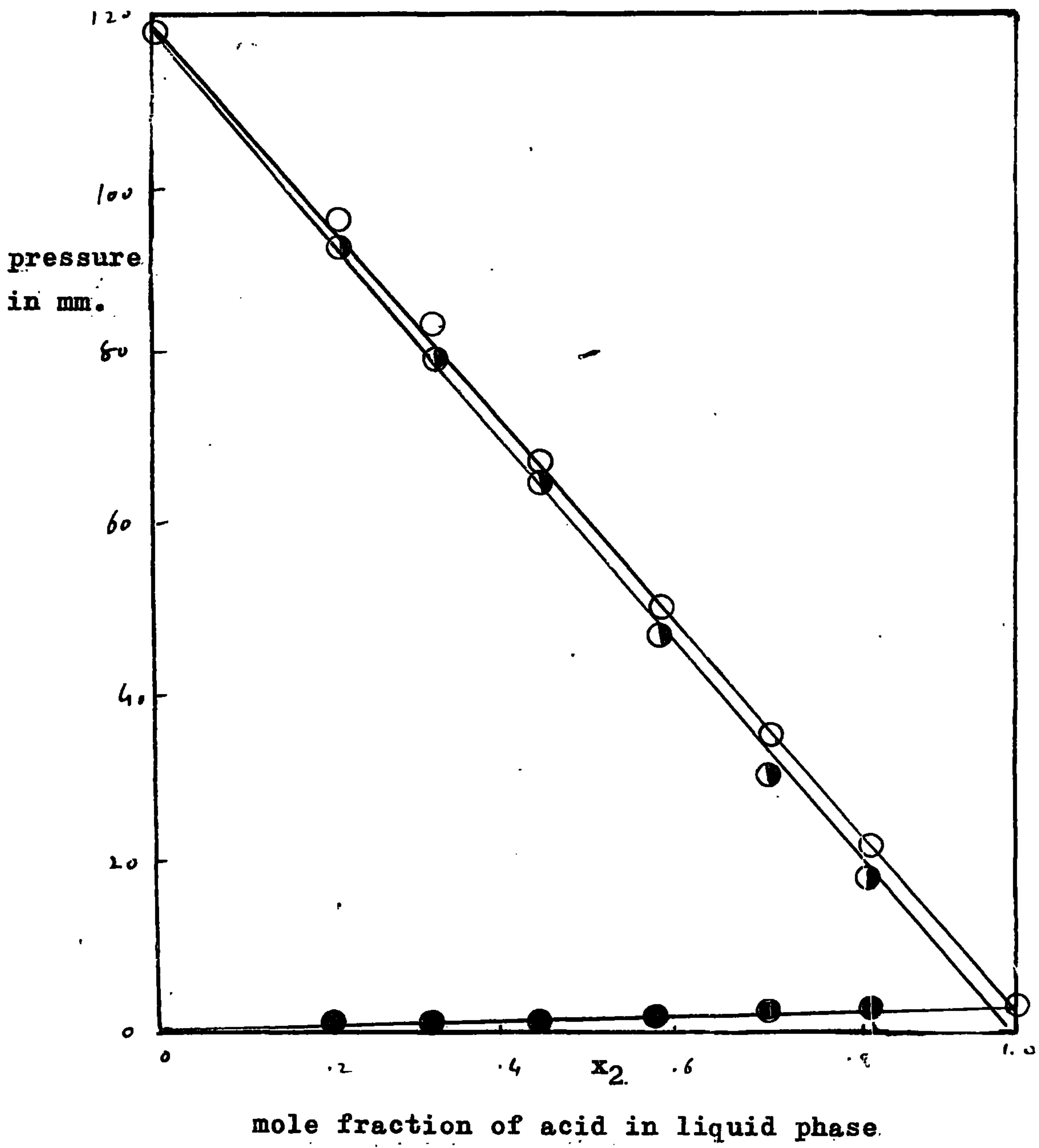
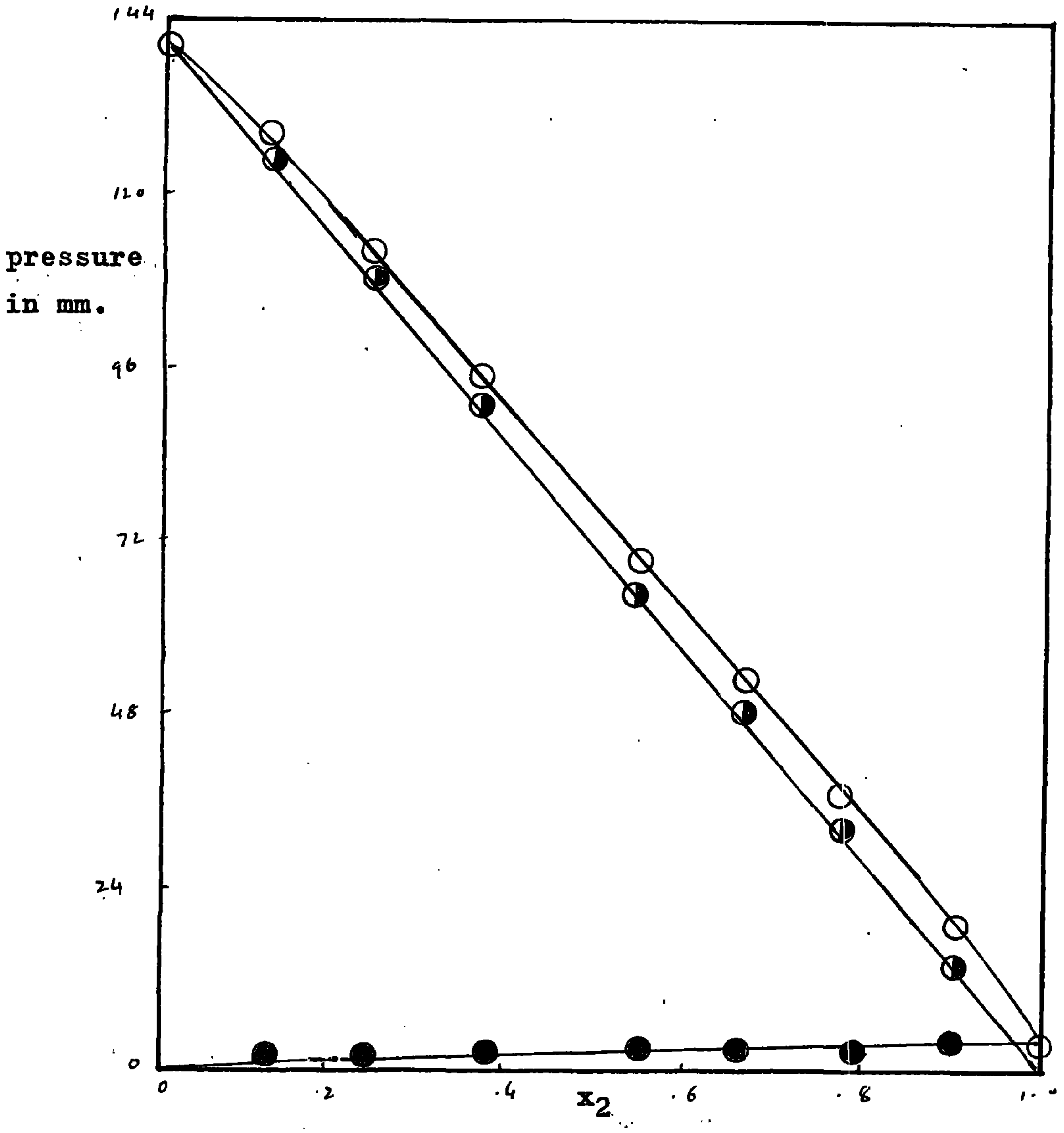


Fig.12–Vapour-pressure curves for butyric acid + benzene system at 30° C.



mole fraction of acid in liquid phase

Fig.13-Vapour-pressure curves for butyric acid + carbon tetrachloride system at 30° C.

TABLE 13.

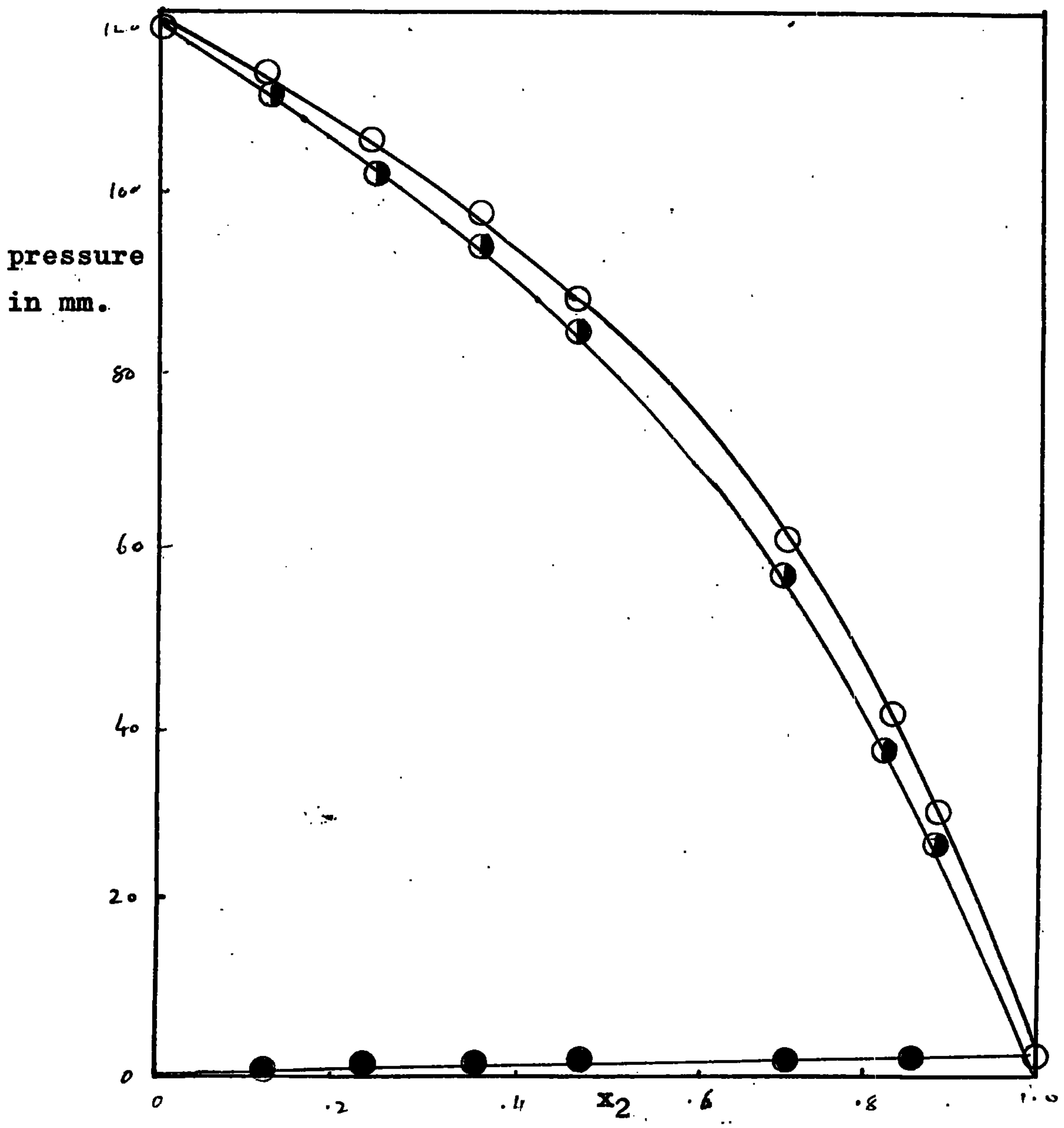
Vapour-Pressure of butyric acid + cyclohexane system.

M.F. of acid	Total Pressure	P.P. of acid	P.P. of cycl.
0.00	121.0 mm	0.0 mm	121.0 mm
0.12	115.0	0.5	113.0
0.24	107.0	0.8	104.0
0.36	99.0	1.0	96.0
0.48	89.0	1.3	86.0
0.60	77.0	1.6	73.0
0.72	63.0	2.0	60.0
0.84	42.0	2.3	38.0
0.96	14.0	2.5	11.0
1.00	2.0	2.0	0.0

TABLE 14.

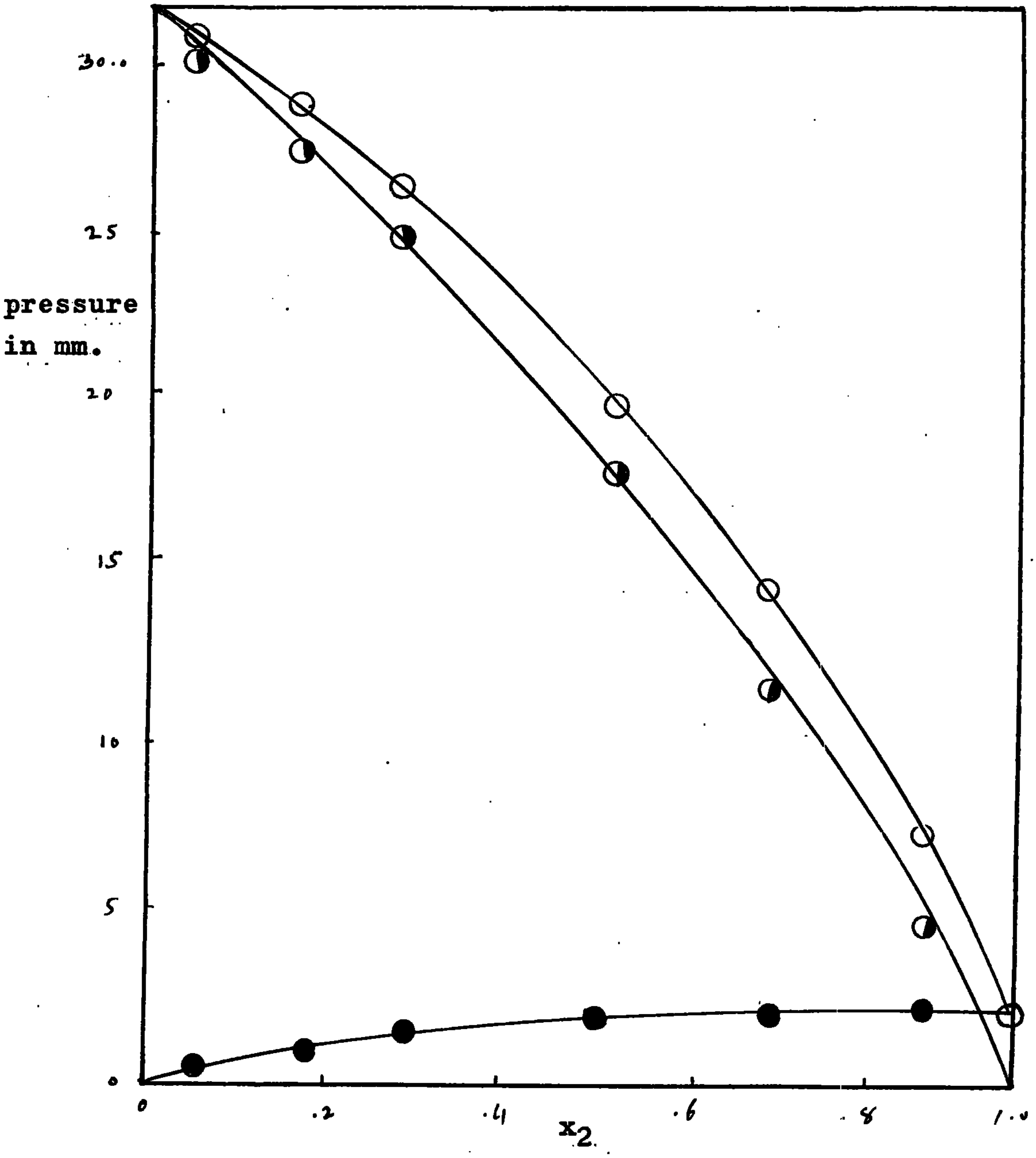
Vapour-Pressure of butyric acid + water system.

M.F. of acid	Total Pressure	P.P. of acid	P.P. of water.
0.00	31.5 mm	0.0 mm	31.0 mm
0.06	30.5	0.5	30.0
0.09	30.0	1.0	29.0
0.18	29.0	1.5	27.5
0.30	26.5	1.8	25.0
0.54	20.0	2.0	18.0
0.72	14.5	2.3	11.5
0.90	7.5	2.5	4.5
1.00	2.0	2.0	0.0



mole fraction of acid in liquid phase

Fig.14-Vapour-pressure curves for butyric acid + cyclohexane system at 30° C.



mole fraction of acid in liquid phase

Fig.15-Vapour-pressure curves for butyric acid + water system at 30° C.

TABLE 15.

Activity coefficient of benzene in acetic acid + benzene system.

$$\ln f_1^l = \ln (p_1 / x_1^l \overset{\circ}{p}_1) - \frac{(B_{11} - \dot{V}_1)(\overset{\circ}{p}_1 - p_T)}{RT}$$

B_{11} = -1.360 litre mole $^{-1}$
V_1° = 0.08994 litre mole $^{-1}$
P_1° = 117.5 mm.
$\phi = \frac{B_{11} - V_1^\circ}{RT} (\overset{\circ}{p}_1 - p_T) = 0.058 (\overset{\circ}{p}_1 - p_T)$

M.F. of benzene x_1^l	Total press. p_T	p_1	$p_1^\circ x_1^l$	$\frac{p_1}{p_1^\circ x_1^l}$	$\log \frac{p_1}{p_1^\circ x_1^l}$	$\ln \frac{p_1}{p_1^\circ x_1^l}$	$\overset{\circ}{p}_1 - p_T$ atmospheric	$-\phi$	$\ln f_1$	$\log f_1$	f_1
0.07	36	15.0	8.22	1.82	0.261	0.601	0.107	0.006	0.607	0.263	1.835
0.11	42	21.8	12.92	1.69	0.228	0.524	0.099	0.006	0.531	0.230	1.70
0.30	62	45.2	35.25	1.284	0.108	0.250	0.073	0.004	0.254	0.110	1.29
0.54	84	73.9	63.45	1.165	0.066	0.153	0.044	0.003	0.155	0.067	1.16
0.72	96	87.0	84.60	1.028	0.009	0.021	0.028	0.002	0.022	0.010	1.03
0.87	108	103.7	102.2	1.015	0.006	0.014	0.012	0.001	0.015	0.007	1.015

TABLE 16.

Activity coefficient of carbon tetrachloride in acetic acid + CCl4 system.

B_{11} = -1.540 litre/mole
V_1^o = 0.0977 litre/mole
P_1^o = 139.5 mm
ϕ = $-0.0658\,(p_1^o - p_T)$

x_1^l	p_T	p_1	$p_1^o x_1^l$	$\frac{p_1}{p_1^o x_1^l}$	$\log \frac{p_1}{p_1^o x_1^l}$	$\ln \frac{p_1}{p_1^o x_1^l}$	$p_1^o - p_T$	$-\phi$	$\ln f_1$	$\log f_1$	f_1
0.10	46	27	13.95	1.93	0.287	0.660	0.123	0.0081	0.6684	0.290	1.950
0.22	70	53	30.70	1.73	0.237	0.546	0.091	0.0060	0.5523	0.240	1.738
0.40	92	79	55.80	1.42	0.151	0.348	0.063	0.0041	0.3518	0.153	1.422
0.60	109	100	83.70	1.19	0.077	0.178	0.040	0.0026	0.1809	0.079	1.197
0.76	122	114	106.02	1.07	0.031	0.073	0.023	0.0015	0.0740	0.032	1.076
0.91	133	129	126.95	1.02	0.028	0.020	0.008	0.0005	0.0200	0.009	1.019

TABLE 17.

Activity coefficient of cyclohexane in acetic acid + cyclohexane system.

B_{11} = -1.575 litre/mole
V_1° = 0.1094 litre/mole
P_1° = 121.5 mm.
ϕ = -0.0677 $(p_1^\circ - p_T)$

x_1^l	p_T	p_1	$p_1^\circ x_1^l$	$\frac{p_1}{p_1^\circ x_1^l}$	$\log \frac{p_1}{p_1^\circ x_1^l}$	$\ln \frac{p_1}{p_1^\circ x_1^l}$	$p_1^\circ - p_T$	$-\phi$	$\ln f_1$	$\log f_1$	f_1
0.10	86	66	12.15	5.43	0.735	1.692	0.048	0.0032	1.6955	0.7362	5.44
0.22	98	78	26.73	2.92	0.465	1.071	0.031	0.0021	1.0729	0.4660	2.92
0.40	108	89	48.6	1.83	0.262	0.605	0.018	0.0012	0.6060	0.2630	1.83
0.52	112	96	63.2	1.52	0.181	0.418	0.012	0.0008	0.4187	0.1818	1.52
0.70	117	106	85.0	1.24	0.095	0.220	0.006	0.0004	0.2203	0.0956	1.24
0.90	123	117	109.4	1.07	0.029	0.067	0.002	0.0001	0.0671	0.0290	1.07

TABLE 18.

Activity coefficient of ethanol in acetic acid + ethanol system.

B_{11}^{o} = -2.920 litre/mole

V_1^{o} = 0.059 litre/mole

P_1^{o} = 78.0 mm

ϕ = $-0.01197\ (p_1^{o} - p_T)$

x_1^{l}	p_T	p_1	$p_1^{o}\ x_1^{l}$	$\frac{p_1}{p_1^{o}x_1^{l}}$	$\log \frac{p_1}{p_1^{o}\ x_1^{l}}$	$\ln \frac{p_1}{p_1^{o}x_1^{l}}$	$p_1^{o} - p_T$	$-\phi$	$\ln f_1$	$\log f_1$	f_1
0.10	26	7.95	7.8	1.019	0.008	0.0184	0.0684	0.0008	0.0192	0.0083	1.020
0.22	33	17.40	17.2	1.014	0.006	0.0138	0.0592	0.0007	0.0145	0.0063	1.015
0.40	43	31.50	31.2	1.009	0.004	0.0096	0.0460	0.0055	0.0100	0.0044	1.010
0.60	55	47.10	46.8	1.006	0.003	0.0062	0.0302	0.004	0.0066	0.0030	1.007
0.76	64	59.50	59.3	1.004	0.002	0.0036	0.0184	0.0002	0.0039	0.0017	1.004
0.90	72	70.30	70.2	1.0014	0.001	0.0014	0.0079	0.0001	0.0015	0.0006	1.002

TABLE 19.

Activity coefficient of water in acetic acid + water system.

B_{11} = -0.630 litre/mole

V_1^o = 0.0181 litre/mole

P_1^o = 31.8 mm.

ϕ = $0.02605\ (p_1^o - p_T)$

x_1^ℓ	p_T	p_1	$p_1^o x_1^\ell$	$\frac{p_1}{p_1^o x_1^\ell}$	$\log \frac{p_1}{p_1^o x_1^\ell}$	$\ln \frac{p_1}{p_1^o x_1^\ell}$	$p_1^o - p_T$	$-\phi$	$\ln f_1$	$\log f_1$	f_1
0.10	21.0	3.25	3.18	1.022	0.0094	0.0216	0.0142	0.0004	0.0220	0.0095	1.022
0.30	23.0	9.70	9.54	1.0168	0.0070	0.0161	0.0116	0.0003	0.0164	0.0071	1.016
0.40	24.5	25.8	12.72	1.0101	0.0044	0.0101	0.0096	0.0002	0.0101	0.0044	1.010
0.50	25.5	16.0	15.9	1.0063	0.0025	0.0057	0.0083	0.0002	0.0059	0.0026	1.006
0.70	28.0	22.3	22.2	1.0040	0.0017	0.0039	0.0050	0.0001	0.0040	0.0017	1.004
0.90	30.5	28.7	28.6	1.0028	0.0011	0.0025	0.0017	0.0001	0.0025	0.0011	1.002

TABLE 20.

Activity coefficient of benzene in propionic acid + benzene system.

B_{11} = −1.360 litre/mole

V_1^o = 0.08994 litre/mole

P_1^o = 117.5 mm

$$\phi = \frac{B_{11}-V_1^o}{RT}(p_1^o - p_T) = 0.0584\,(p_1^o - p_T)$$

x_1^l	p_T	p_1	$p_1^o x_1^l$	$\frac{p_1}{p_1^o x_1^l}$	$\log \frac{p_1}{p_1^o x_1^l}$	$\ln \frac{p_1}{p_1^o x_1^l}$	$p_1^o - p_T$	$-\phi$	$\ln f_1$	$\log f_1$	f_1
0.02	6	3.2	2.35	1.37	0.173	0.400	0.147	0.0085	0.407	0.1766	1.382
0.14	24	20.5	16.45	1.25	0.096	0.220	0.123	0.0072	0.227	0.0985	1.255
0.39	54	52.4	45.82	1.14	0.058	0.133	0.083	0.0049	0.138	0.0600	1.148
0.65	80	78.6	76.37	1.03	0.013	0.029	0.049	0.0029	0.032	0.0138	1.033
0.79	96	94.5	92.82	1.02	0.007	0.017	0.028	0.0016	0.019	0.0083	1.020
0.92	110	109	108.33	1.005	0.002	0.005	0.010	0.0006	0.005	0.0022	1.006

TABLE 21.

Activity coefficient of carbon tetrachloride in propionic acid + CCl_4 system.

B_{11} = 1.540 litre/mole
V_1^o = 0.0977 litre/mole
P_1^o = 139.5 mm.
ϕ = 0.0658 $(p_1^o - p_T)$

x_1^l	p_T	p_1	$p_1^o x_1^l$	$\frac{p_1}{p_1^o x_1^l}$	log $\frac{p_1}{p_1^o x_1^l}$	ln $\frac{p_1}{p_1^o x_1^l}$	$p_1^o - p_T$	$1 - \phi$	ln f_1	log f_1	f_1
0.10	31	25	13.95	1.792	0.253	0.5828	0.143	0.0094	0.592	0.257	1.807
0.22	48	43	30.69	1.401	0.146	0.3371	0.120	0.0079	0.345	0.150	1.413
0.40	70	65	55.80	1.165	0.066	0.1517	0.091	0.0060	0.158	0.068	1.169
0.60	93	89	83.70	1.063	0.026	0.0610	0.061	0.0040	0.065	0.028	1.067
0.76	113	109	106	1.033	0.014	0.032	0.0348	0.0023	0.034	0.015	1.035
0.91	130	128	127	1.016	0.007	0.015	0.0125	0.0008	0.016	0.007	1.016

TABLE 22.

Activity coefficient of cyclohexane in propionic acid + cyclohexane system.

B_{11} = 1.575 litre/mole

V_1^o = 0.1094 litre/mole

p_1^o = 121.5 mm

ϕ -0.0677 $(p_1^o - p_T)$

x_1^l	p_T	p_1	$p_1^o x_1^l$	$\frac{p_1}{p_1^o x_1^l}$	$\log \frac{p_1}{p_1^o x_1^l}$	$\ln \frac{p_1}{p_1^o x_1^l}$	$p_1^o - p_T$	$-\phi$	$\ln f_1$	$\log f_1$	f_1
0.10	42	24	12.15	1.990	0.2989	0.593	0.1046	0.007	0.600	0.2661	1.905
0.28	77	63	34.02	1.853	0.2678	0.529	0.0580	0.007	0.587	0.2550	1.850
0.40	90	80	48.60	1.647	0.216	0.503	0.041	0.003	0.506	0.2197	1.66
0.52	99	92	63.18	1.456	0.163	0.377	0.029	0.002	0.379	0.1647	1.461
0.70	108	104	85.05	1.222	0.087	0.201	0.018	0.001	0.202	0.0879	1.224
0.91	118	116	110.56	1.049	0.021	0.021	0.048	0.0003	0.048	0.0209	1.049

TABLE 23.

Activity coefficient of ethanol in propionic acid + ethanol system.

$B_{11} = -2.920$ litre/mole

$V_1^{\ell} = 0.059$ litre/mole

$P_1^{o} = 78.0$ mm

$\phi = -0.01197\ (p_1^{o} - p_T)$

x_1^{ℓ}	p_T	p_1	$p_1^{o} x_1^{\ell}$	$\frac{p_1}{p_1^{o} x_1^{\ell}}$	$\log \frac{p_1}{p_1^{o} x_1^{\ell}}$	$\ln \frac{p_1}{p_1^{o} x_1^{\ell}}$	$p_1^{o} - p_T$	$-\phi$	$\ln f_1$	$\log f_1$	f_1
0.10	11.5	8.00	7.80	1.026	0.110	0.0251	0.0875	0.0010	0.0261	0.0113	1.027
0.22	21.0	17.5	17.16	1.020	0.0086	0.0198	0.0750	0.0009	0.0210	0.0090	1.021
0.40	34.0	31.6	31.20	1.013	0.0055	0.0127	0.0579	0.0007	0.0130	0.0058	1.014
0.60	49.5	47.2	46.80	1.009	0.0042	0.0097	0.0375	0.0005	0.0101	0.0044	1.010
0.76	61.0	59.3	59.60	1.005	0.0023	0.0053	0.0223	0.0003	0.0055	0.0024	1.006
0.91	72.0	71.1	70.98	1.0016	0.0006	0.0015	0.0079	0.0001	0.0016	0.0007	1.002

TABLE 24.

Activity coefficient of water in propionic acid + water system.

B_{11} = -0.630 litre/mole
V_1° = 0.0181 litre/mole
P_1° = 31.8 mm.
ϕ = 0.02605 ($p_1^\circ - p_T$)

x_1^l	p_T	p_1	$p_1^\circ x_1^l$	$\frac{p_1}{p_1^\circ x_1^l}$	$\log \frac{p_1}{p_1^\circ x_1^l}$	$\ln \frac{p_1}{p_1^\circ x_1^l}$	$p_1^\circ - p_T$	$-\phi$	$\ln f_1$	$\log f_1$	f_1
0.10	11	4.5	3.18	1.405	0.1507	0.3470	0.0274	0.0007	0.3477	0.1510	1.416
0.20	14	7.4	6.36	1.163	0.0656	0.1511	0.0234	0.0006	0.1516	0.0658	1.164
0.40	20.5	13.75	12.7	1.081	0.0335	0.0771	0.0148	0.0004	0.775	0.0336	1.081
0.60	23.5	19.75	19.1	1.035	0.0149	0.0343	0.0109	0.0003	0.0346	0.0150	1.035
0.75	26.5	24.25	23.8	1.0168	0.0070	0.0161	0.0070	0.0002	0.0163	0.0071	1.016
0.91	30.0	29.10	28.9	1.0055	0.0023	0.0053	0.0023	0.0001	0.0053	0.0023	1.006

TABLE 25.

Activity coefficients of benzene in butyric acid + benzene system.

B_{11} = -1.360 litre/mole

$V_1^{\prime}$ = 0.08994 litre/mole

p_1^0 = 117.5 mm.

$$\phi = \frac{B_{11}-V_1^0}{RT}\,(p_1^0 - p_T) = 0.0583\,(p_1^0 - p_T)$$

x_1^l	p_T	p_1	$p_1^0 x_1^l$	$\frac{p_1}{p_1^0 x_1^l}$	$\log \frac{p_1}{p_1^0 x_1^l}$	$\ln \frac{p_1}{p_1^0 x_1^l}$	$p_1^0 - p_T$	$-\phi$	$\ln f_1$	$\log f_1$	f_1
0.05	7	5.5	5.3	1.040	0.017	0.039	0.145	0.0085	0.0476	0.0192	1.049
0.29	36	35.3	34.1	1.035	0.015	0.034	0.107	0.0062	0.0410	0.0178	1.040
0.54	66	64.7	63.4	1.019	0.008	0.018	0.067	0.0039	0.0226	0.0098	1.023
0.68	82	80.8	79.9	1.011	0.005	0.011	0.046	0.0027	0.0135	0.0058	1.014
0.79	94	93.5	92.8	1.008	0.003	0.007	0.030	0.0017	0.0091	0.0039	1.009
0.91	108	107.5	107.1	1.003	0.001	0.002	0.012	0.0007	0.0032	0.0014	1.003

TABLE 26.

Activity coefficient of carbon tetrachloride in butyric acid + CCl_4 system.

B_{11} = -1.540 litre per mole

V_1^0 = 0.0977 litre per mole

p_1^0 = 139.5 mm.

ϕ = $0.0658\ (p_1^0 - p_T)$.

x_1^0	p_T	p_1	$p_1^0 x_1^l$	$\frac{p_1}{p_1^0 x_1^l}$	$\log \frac{p_1}{p_1^0 x_1^l}$	$\ln \frac{p_1}{p_1^0 x_1^l}$	$p_1^0 - p_T$	$-\phi$	$\ln f_1$	$\log f_1$	f_1
0.10	18	14.5	13.95	1.039	0.017	0.0387	0.160	0.0105	0.049	0.021	1.051
0.22	35	31.6	30.69	1.026	0.011	0.0255	0.137	0.0090	0.034	0.015	1.035
0.40	60	57.0	55.80	1.021	0.009	0.0212	0.104	0.0069	0.028	0.012	1.028
0.60	88	85.0	83.70	1.015	0.006	0.0152	0.068,	0.0044	0.0196	0.008	1.020
0.76	110	107.5	106.0	1.011	0.005	0.0113	0.039	0.0025	0.0140	0.006	1.014
0.91	130	127.8	126.9	1.007	0.003	0.0080	0.012	0.0008	0.0070	0.004	1.009

TABLE 27.

Activity coefficient of cyclohexane in butyric acid + cyclohexane system.

B_{11} = −1.575 litre/mole

V_1° = 0.1094 litre/mole

p° = 121.5 mm.

$\phi = -0.0677\,(p_1^\circ - p_T)$

x_1^l	p_T	p_1	$p_1^\circ x_1^l$	$\frac{p_1}{p_1^\circ x_1^l}$	$\log \frac{p_1}{p_1^\circ x_1^l}$	$\ln \frac{p_1}{p_1^\circ x_1^l}$	$p_1^\circ - p_T$	$-\phi$	$\ln f_1$	$\log f_1$	f_1
0.10	29	22	12.15	1.810	0.2577	0.610	0.122	0.008	0.768	0.3337	1.830
0.22	54	44	28.73	1.641	0.2164	0.498	0.088	0.006	0.504	0.2189	1.655
0.40	77	74	48.6	1.522	0.1820	0.420	0.058	0.004	0.424	0.1840	1.528
0.52	89	86	63.2	1.379	0.1360	0.314	0.043	0.003	0.0317	0.1370	1.373
0.70	103	101	85.1	1.187	0.074	0.171	0.024	0.002	0.172	0.074	1.187
0.91	116	115	110.5	1.040	0.017	0.038	0.007	0.005	0.040	0.017	1.040

TABLE 28.

Activity coefficient of water in butyric acid + water system.

B_{11} = -0.630 litre/mole

V_1^o = 0.0181 litre/mole

P_1^o = 31.8 mm.

ϕ = 0.02605 $(p_1^o - p_T)$

x_1^ℓ	p_T	p_1	$p_1^o x_1^\ell$	$\frac{p_1}{p_1^o x_1^\ell}$	$\log \frac{p_1}{p_1^o x_1^\ell}$	$\ln \frac{p_1}{p_1^o x_1^\ell}$	$p_1 - p_T$	$-\phi$	$\ln f_1$	$\log f_1$	f_1
0.10	7.5	4.75	3.18	1.494	0.1742	0.4012	0.0320	0.0008	0.4020	0.1745	1.495
0.20	12.0	8.50	6.36	1.336	0.1260	0.2897	0.0260	0.0007	0.2903	0.1260	1.337
0.40	18.5	16.0	12.72	1.258	0.0993	0.2287	0.0175	0.0004	0.2291	0.0995	1.258
0.60	24.0	22.5	19.08	1.179	0.0716	0.1648	0.0104	0.0003	0.1650	0.0717	1.179
0.75	27.0	26.0	23.85	1.090	0.0374	0.0861	0.0063	0.0002	0.0863	0.0374	1.090
0.91	30.0	29.5	28.94	1.019	0.0081	0.0186	0.0024	0.0001	0.0187	0.0081	1.019

TABLE 29.

Activity coefficients of acid in acetic acid + benzene system.

M.F. of acid x_2	M.F. of benz. x_1	$\frac{x_1}{x_2}$	ln f_1 at x_1	x_2	$\frac{x_1}{x_2}$	ln f_2	log f_2	f_2 act. coefft.
0.13	0.87	6.69	0.01	0.1	9.0	0.11	0.05	1.116
0.28	0.72	2.57	0.03	0.2	4.0	0.17	0.07	1.185
0.46	0.54	1.17	0.15	0.3	2.3	0.25	0.11	1.286
0.70	0.30	0.43	0.25	0.4	1.5	0.37	0.16	1.447
0.89	0.11	0.12	0.53	0.5	1.0	0.45	0.19	1.568
0.93	0.07	0.07	0.66	0.7	0.4	0.57	0.24	1.765
0.95	0.05	0.05	0.70	0.9	0.11	0.60	0.27	1.866

TABLE 30.

Activity coeeffts. of acid in acetic acid + carbon tet. system.

M.F. of acid x_2	M.F. of CCl_4 x_1	$\frac{x_1}{x_2}$	ln f_1 at x_1	x_2	$\frac{x_1}{x_2}$	ln f_2	log f_2	f_2 act.
0.09	0.91	10.11	0.02	0.1	9.0	0.31	0.13	1.367
0.24	0.76	3.16	0.07	0.2	4.0	0.51	0.22	1.593
0.40	0.60	1.50	0.18	0.4	1.5	0.80	0.35	2.236
0.60	0.40	0.66	0.35	0.5	1.0	0.88	0.38	2.430
0.78	0.22	0.28	0.55	0.7	0.4	1.07	0.47	2.900
0.90	0.10	0.11	0.66	0.9	0.1	1.32	0.57	3.750

TABLE 31.

Activity coeffts. of acid in acetic acid +cyclohexane system.

M.F of acid x_2	M.F. of cycl. x_1	$\frac{x_1}{x_2}$	ln f at x_1	x_2	$\frac{x_1}{x_2}$	ln f_2	log f_2	f_2
0.10	0.90	9.00	0.067	0.1	9.0	0.64	0.278	1.89
0.30	0.70	2.30	0.220	0.2	4.0	1.18	0.512	1.25
0.48	0.52	1.08	0.418	0.3	2.33	1.38	0.600	3.98
0.60	0.40	0.66	0.605	0.5	1.0	1.73	0.751	5.60
0.78	0.22	0.28	0.999	0.7	0.4	1.90	0.825	6.68
0.90	0.10	0.11	0.691	0.9	0.1	1.99	0.862	7.32

TABLE 32.

Activity coeffts. of acid in acetic acid + ethanol system.

M.F. of acid x_2	M.F. of eth. x_1	$\frac{x_1}{x_2}$	ln f_1 at x_1	x_2	$\frac{x_1}{x_2}$	ln f_2	log f_2	f_2
0.10	0.90	9.0	0.002	0.1	9.0	0.020	0.007	1.016
0.24	0.76	3.1	0.004	0.2	4.0	0.025	0.011	1.026
0.40	0.60	1.5	0.007	0.3	2.3	0.031	0.013	0.031
0.60	0.40	0.6	0.010	0.5	1.0	0.035	0.015	1.037
0.78	0.22	0.3	0.015	0.7	0.4	0.040	0.017	1.041
0.90	0.10	0.1	0.019	0.9	0.1	0.042	0.018	1.042

TABLE 33.

Activity coeffts. of acid in acetic acid + water system.

M.F. of acid x_2	M.F. of water x_1	$\frac{x_1}{x_2}$	ln f at x_1	x_2	$\frac{x_1}{x_2}$	ln f_2	log f_2	f_2
0.10	0.90	9.00	0.003	0.1	9.0	0.032	0.014	1.033
0.30	0.70	2.33	0.004	0.2	4.0	0.039	0.017	1.042
0.50	0.50	1.00	0.006	0.3	2.3	0.041	0.018	1.043
0.60	0.40	0.66	0.010	0.5	1.0	0.045	0.022	1.046
0.70	0.30	0.42	0.016	0.7	0.4	0.051	0.022	1.052
0.90	0.10	0.11	0.022	0.9	0.1	0.052	0.023	1.054

TABLE 34.

Activity coeffts. of acid in propionic acid + benzene system.

M.F. of acid x_2	M.F. of benz.x_1	$\frac{x_1}{x_2}$	ln f_1 at x_1	x_2	$\frac{x_1}{x_2}$	ln f_2	log f_2	f_2
0.08	0.92	11.50	0.005	0.1	9.0	0.08	0.035	1.08
0.21	0.79	3.76	0.020	0.2	4.0	0.14	0.063	1.15
0.35	0.65	1.85	0.032	0.3	2.3	0.17	0.076	1.19
0.61	0.39	0.64	0.138	0.5	1.0	0.24	0.104	1.27
0.86	0.14	0.16	0.268	0.7	0.4	0.29	0.126	1.34
0.98	0.02	0.02	0.408	0.9	0.1	0.31	0.135	1.36

TABLE 35.

Activity coeffts. of acid in propionic acid + carbon tet. system.

M.F. of acid x_2	M.F. of $CCl_4 x_1$	$\frac{x_1}{x_2}$	ln f_1 at x_1	x_2	$\frac{x_1}{x_2}$	ln f_2	log f_2	f_2
0.09	0.91	10.1	0.016	0.1	9.0	0.14	0.06	1.15
0.24	0.76	3.16	0.035	0.2	4.0	0.19	0.08	1.21
0.40	0.60	1.50	0.065	0.3	2.3	0.27	0.11	1.31
0.60	0.40	0.66	0.157	0.5	1.0	0.35	0.15	1.42
0.78	0.22	0.28	0.340	0.7	0.4	0.44	0.19	1.55
0.90	0.10	0.11	0.59	0.9	0.1	0.51	0.22	1.66

TABLE 36.

Activity coeffts. of acid in propionic acid + cyclohexane system.

M.F. of acid x_2	M.F. of cyc. x_1	$\frac{x_1}{x_2}$	ln f_1 at x_1	x_2	$\frac{x_1}{x_2}$	ln f_2	log f_2	f_2
0.09	0.91	10.11	0.048	0.1	9.0	0.61	0.26	1.85
0.30	0.70	2.33	0.203	0.2	4.0	0.99	0.47	2.98
0.48	0.52	1.08	0.399	0.3	2.3	1.26	0.55	3.54
0.60	0.40	0.66	0.537	0.5	1.0	1.54	0.67	4.68
0.72	0.28	0.39	0.740	0.7	0.4	1.70	0.73	5.43
0.90	0.10	0.10	1.140	0.9	0.1	1.76	0.76	5.84

TABLE 37.

Activity coeffts. of acid in propionic acid + ethanol system.

M.F. of acid x_2	M.F. of eth. x_1	$\frac{x_1}{x_2}$	ln f_1 at x_1	x_2	$\frac{x_1}{x_2}$	ln f_2	log f_2	f_2
0.09	0.91	10.11	0.001	0.1	9.0	0.01	0.004	1.010
0.24	0.76	3.16	0.002	0.2	4.0	0.015	0.007	1.020
0.40	0.60	1.50	0.004	0.3	2.3	0.025	0.010	1.025
0.60	0.40	0.66	0.006	0.5	1.0	0.027	0.012	1.029
0.78	0.22	0.28	0.009	0.7	0.4	0.029	0.013	1.030
0.90	0.10	0.11	0.011	0.9	0.1	0.030	0.013	1.031

TABLE 38.

Activity coeffts. of acid in propionic acid + water system.

M.F. of acid x_2	M.F. of water x_1	$\frac{x_1}{x_2}$	ln f_1 at x_1	x_2	$\frac{x_1}{x_2}$	ln f_2	log f_2	f_2
0.09	0.91	10.11	0.005	0.1	9.0	0.104	0.04	1.11
0.25	0.75	3.00	0.016	0.2	4.0	0.124	0.05	1.13
0.40	0.60	1.50	0.034	0.3	2.3	0.151	0.06	1.16
0.60	0.40	0.66	0.077	0.5	1.0	0.189	0.08	1.21
0.80	0.20	0.25	0.151	0.7	0.4	0.238	0.10	1.26
0.90	0.10	0.11	0.347	0.9	0.1	0.247	0.11	1.28

TABLE 39.

Activity coeffts. of acid in butyric acid + benzene system.

M.F. of acid x_2	M.F. of benz. x_1	$\frac{x_1}{x_2}$	ln f_1 at x_1	x_2	$\frac{x_1}{x_2}$	ln f_2	log f_2	f_2
0.09	0.91	10.11	0.003	0.1	9.0	0.048	0.021	1.05
0.21	0.79	3.76	0.009	0.2	4.0	0.078	0.034	1.08
0.32	0.68	2.12	0.013	0.3	2.3	0.090	0.039	1.09
0.46	0.54	1.17	0.022	0.5	1.0	0.107	0.046	1.11
0.71	0.29	0.41	0.041	0.7	0.4	0.117	0.051	1.12
0.90	0.10	0.11	0.052	0.9	0.1	0.121	0.052	1.13

TABLE 40.

Activity coeffts. of acid in butyric acid + CCl_4 system

M.F. of acid x_2	M.F. of CCl_4 x_1	$\frac{x_1}{x_2}$	ln f_1 at x_1	x_2	$\frac{x_1}{x_2}$	ln f_2	log f_2	f_2
0.09	0.91	10.11	0.007	0.1	9.0	0.105	0.045	1.11
0.24	0.76	3.16	0.014	0.2	4.0	0.136	0.059	1.14
0.40	0.60	1.50	0.019	0.3	2.3	0.178	0.077	1.19
0.60	0.40	0.66	0.028	0.5	1.0	0.190	0.080	1.20
0.78	0.22	0.28	0.034	0.7	0.4	0.196	0.085	1.21
0.90	0.10	0.11	0.049	0.9	0.1	0.199	0.086	1.22

TABLE 41.

Activity coeffts. of acid in butyric acid + cyclohexane system.

M.F. of acid x_2	M.F. of cyc. x_1	$\frac{x_1}{x_2}$	ln f_1 at x_1	x_2	$\frac{x_1}{x_2}$	ln f_2	log f_2	f_2
0.09	0.91	10.11	0.04	0.1	9.0	0.530	0.230	1.70
0.30	0.70	2.33	0.17	0.2	4.0	0.980	0.425	2.66
0.48	0.52	1.08	0.32	3.0	2.3	1.120	0.486	3.06
0.60	0.40	0.66	0.42	5.0	1.0	1.360	0.592	3.91
0.78	0.22	0.28	0.63	7.0	0.4	1.480	0.646	4.42
0.90	0.10	0.11	0.76	9.0	0.1	1.510	0.655	4.52

TABLE 42.

Activity coeffts. of acid in butyric acid + water system.

M.F. of acid x_2	M.F. of water x_1	$\frac{x_1}{x_2}$	ln f_1 at x_1	x_2	$\frac{x_1}{x_2}$	ln f_2	log f_2	f_2
0.09	0.91	10.11	0.018	0.1	9.0	0.28	0.123	1.33
0.25	0.75	3.00	0.086	0.2	4.0	0.53	0.232	1.70
0.40	0.60	1.50	0.165	0.3	2.3	0.65	0.282	1.91
0.60	0.40	0.66	0.229	0.5	1.0	0.76	0.332	2.15
0.80	0.20	0.25	0.290	0.7	0.4	0.81	0.351	2.25
0.90	0.10	0.11	0.402	0.9	0.1	0.84	0.367	2.32

TABLE 43.

Surface excess in acetic acid + benzene system.

$$\Gamma_2^N = \frac{-x_1}{RT} \frac{d\gamma}{d \ln a_2}$$

$R = 8.3144 \times 10^7$ dynes/cm^2/mole

$RT = 2.519 \times 10^{10}$

m_2 = molarity

M.F. acid x_2	M.F. benz. x_1	m_2	f_2	activity $a_2 = m_2f_2$	$\log a_2$	$\ln a_2$	$\frac{x_1}{RT}$ $\times 10^{-10}$	γ_{30} Dyne/cm	$\frac{d\gamma}{d\ln a_2}$	Γ_2^N μ moles/sq. m.
0.07	0.93	1.5	1.08	1.62	0.21	0.5	0.369	27.10	0.457	+0.169
0.11	0.89	2.4	1.11	2.65	0.42	1.0	0.353	26.70	0.514	+0.175
0.21	0.79	4.3	1.21	5.20	0.71	1.6	0.314	26.40	0.600	+0.188
0.32	0.68	6.3	1.31	8.33	0.92	2.1	0.270	26.00	0.630	+0.170
0.41	0.59	8.1	1.41	11.36	1.05	2.4	0.234	25.80	0.646	+0.151
0.52	0.48	9.9	1.55	15.37	1.18	2.7	0.191	25.56	0.308	+0.056
0.66	0.34	12.3	1.64	20.20	1.30	3.0	0.133	25.68	0.862	+0.114
0.78	0.22	14.0	1.75	24.63	1.39	3.2	0.088	25.91	1.231	-0.110
0.87	0.13	15.4	1.83	28.17	1.45	3.3	0.052	26.10	1.476	-0.077

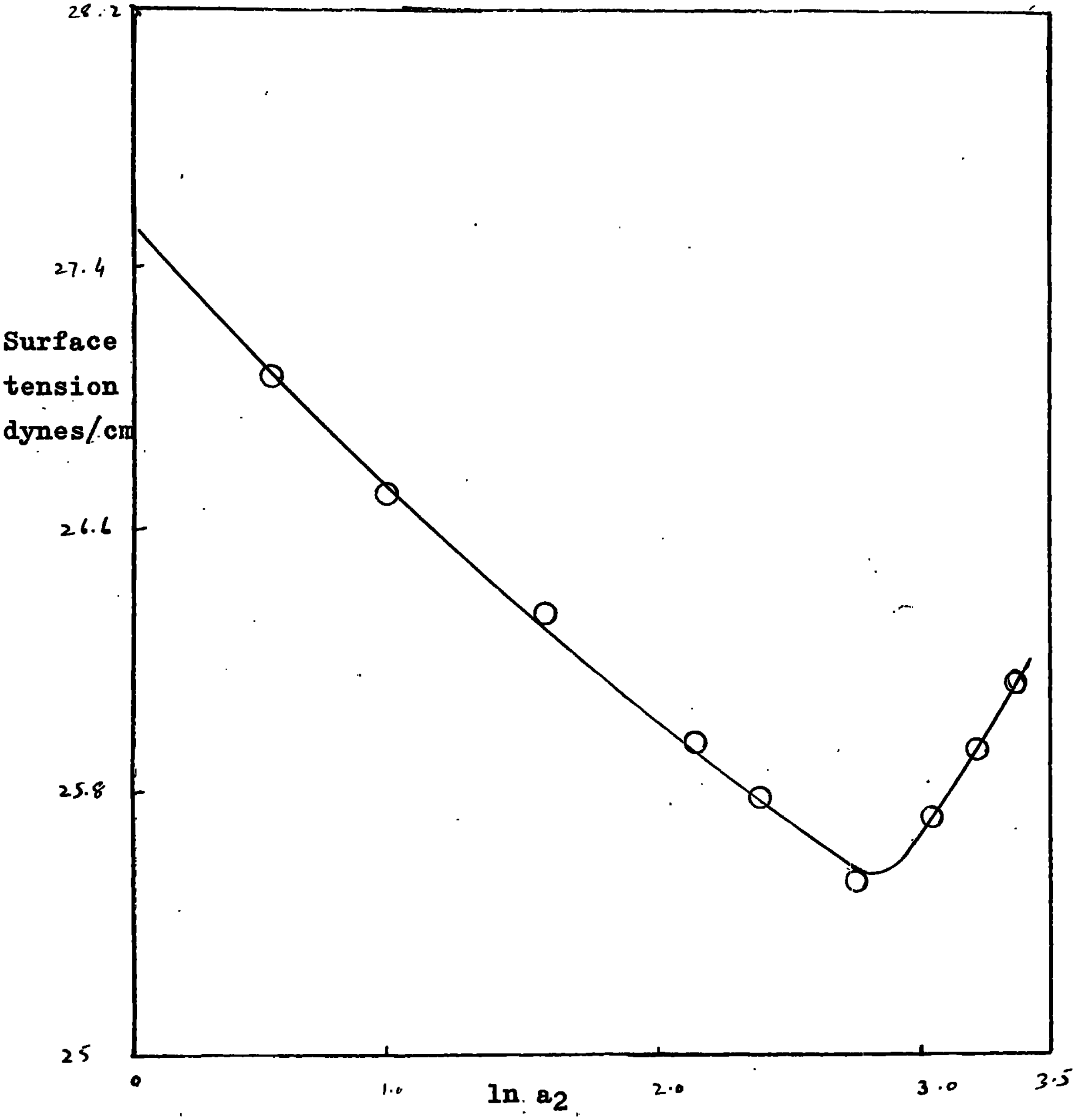


Fig.16-Plot of ln a_2 against surface tension of acetic acid + benzene system at 30 C.

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2P

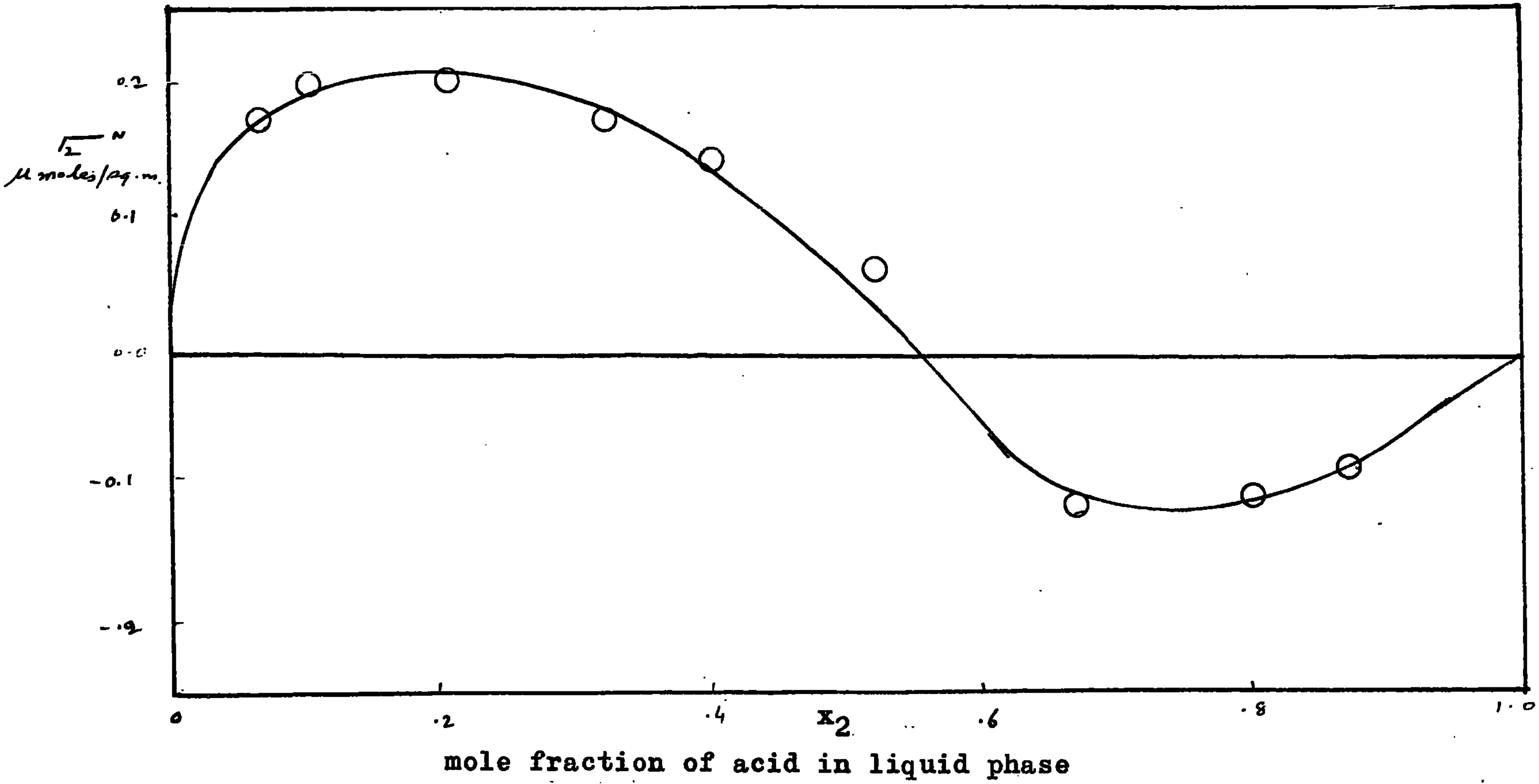

Fig.17- Composite isotherm showing surface excess in acetic acid + benzene system at the solution-vapour interface.

TABLE 44.

Surface excess in acetic acid + carbon tetrachloride system.

$R = 8.3144 \times 10^7$ dynes/cm^2/mole.

$RT = 2.5190 \times 10^{10}$

x_2	x_1	m_2	f_2	a_2	log a_2	ln a_2	$\frac{x_1}{RT}$ $\times 10^{-10}$	γ Dynes/cm	$\frac{d\gamma}{d\ln a_2}$	μ moles/sq.m. Γ_2 ~
0.15	0.85	3.0	1.48	4.46	0.650	1.49	0.336	25.00	0.30	+0.100
0.30	0.70	5.7	1.90	10.88	1.036	2.38	0.278	24.82	0.20	+0.056
0.33	0.67	6.4	1.99	12.72	1.105	2.54	0.264	24.62	0.053	+0.015
0.42	0.58	8.0	2.24	17.92	1.253	2.88	0.228	24.86	0.50	-0.114
0.54	0.46	9.9	2.54	25.30	1.403	3.21	0.183	25.01	1.12	-0.20
0.60	0.40	11.0	2.69	29.5	1.470	3.38	0.158	25.30	1.21	-0.191
0.73	0.27	13.0	3.06	39.90	1.601	3.68	0.108	25.68	1.33	-0.144
0.91	0.09	15.9	3.63	57.70	1.760	4.05	0.036	26.00	2.00	-0.067

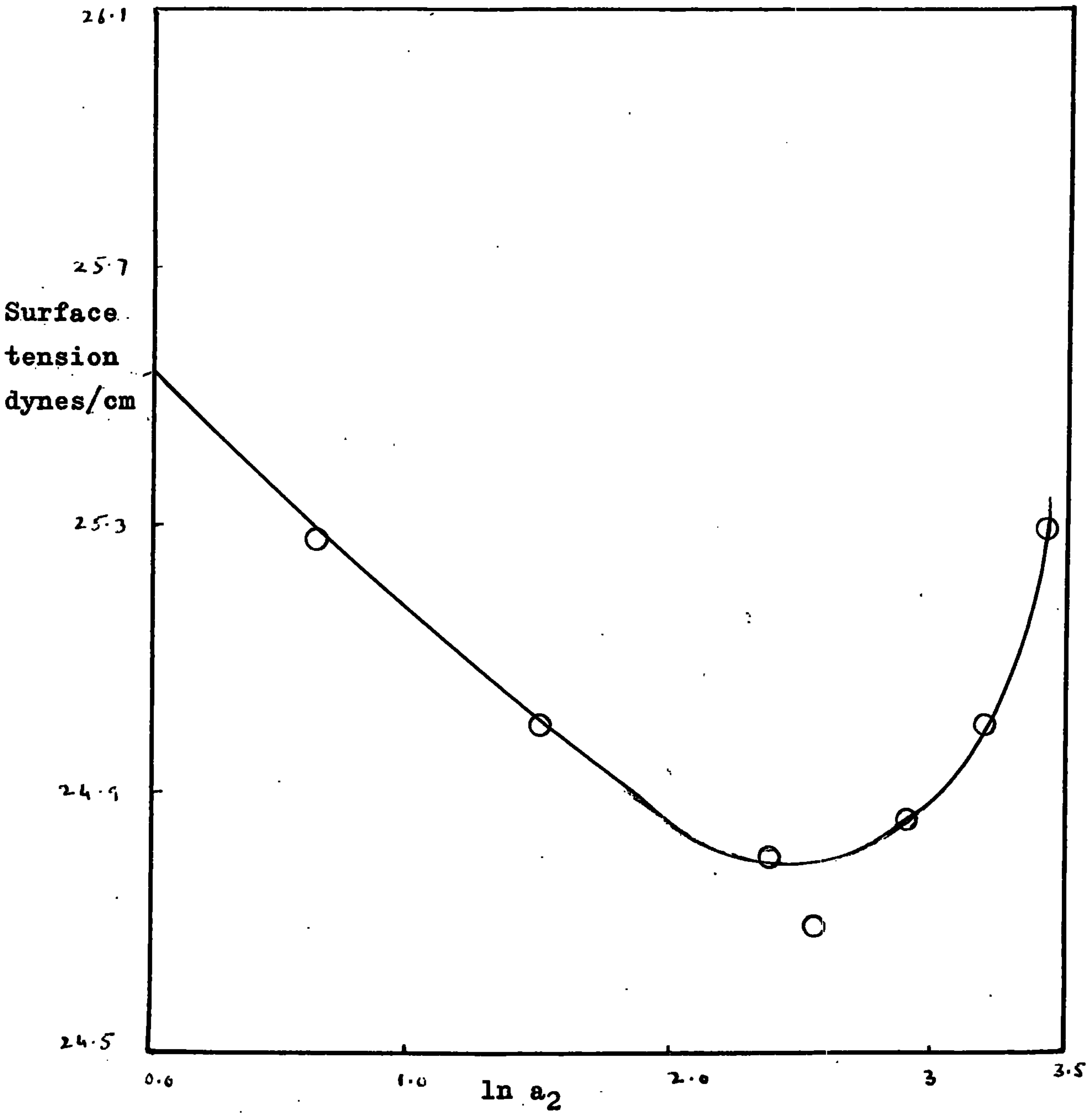

Fig.18-Plot of ln a_1 against surface tension of acetic acid + carbon tetrachloride system at 30° C.

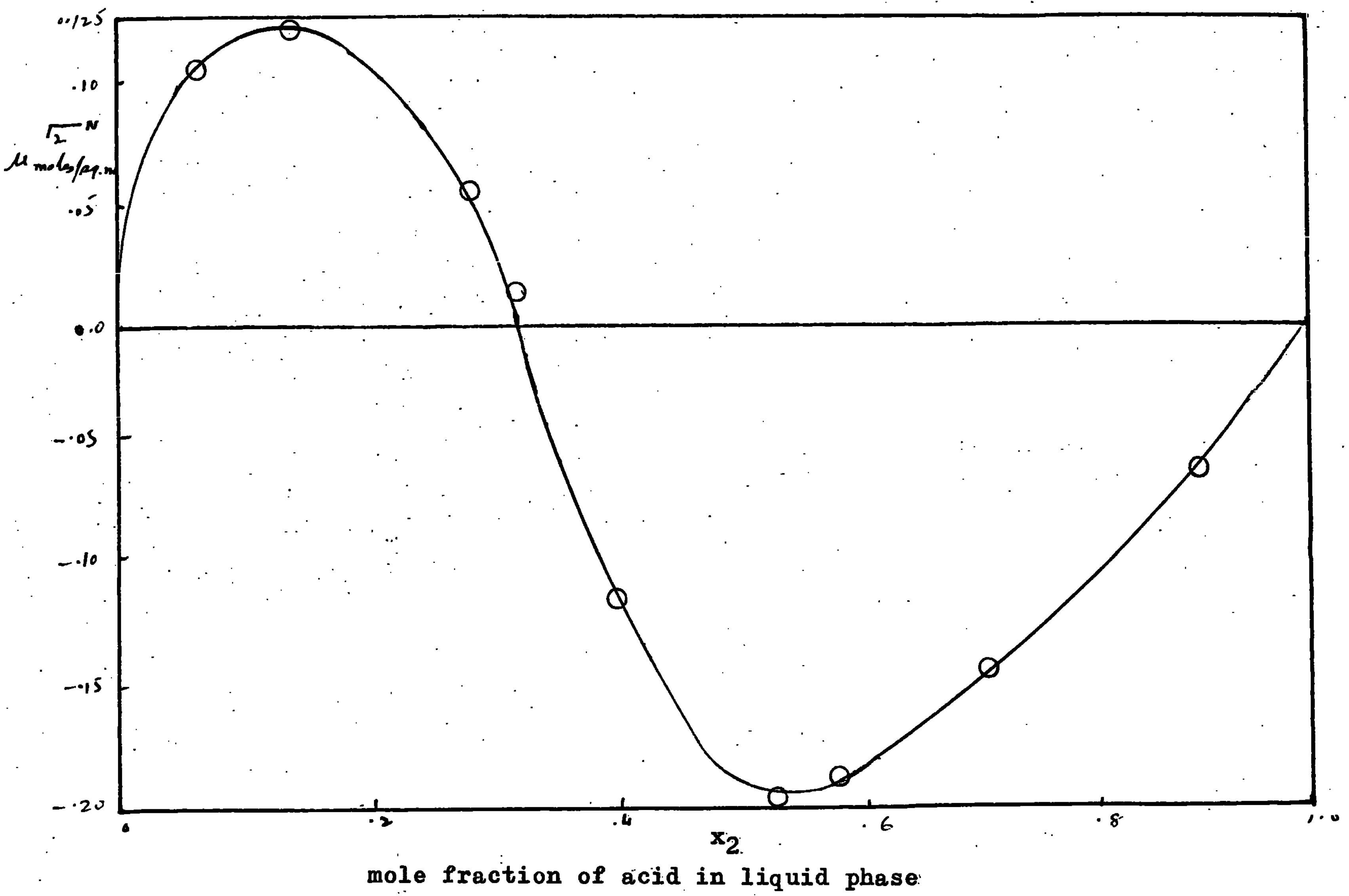

Fig.19- Composite isotherm showing surface excess in acetic acid + carbon tetrachloride system at the solution-vapour interface.

TABLE 45.

Surface excess in acetic acid + cyclohexane system.

x_2	x_1	m_2	f_2	a_2	log a_2	ln a_2	$\frac{x_1}{RT} \times 10^{-10}$	γ Dynes/cm	$\frac{d\gamma}{d\ln a_2}$	μmoles/sq.m. Γ_2^N
0.11	0.89	1.12	2.00	2.24	0.35	0.90	0.353	23.77	0.20	+0.071
0.29	0.71	3.06	4.00	12.25	1.08	2.50	0.280	23.60	0.22	+0.061
0.46	0.54	5.30	5.25	27.84	1.44	3.33	0.214	23.46	0.20	+0.043
0.57	0.43	7.04	5.95	41.87	1.62	3.73	0.170	23.40	0.04	+0.007
0.68	0.32	9.16	6.45	59.10	1.77	4.08	0.128	23.56	0.80	-0.120
0.81	0.19	11.84	7.00	82.91	1.92	4.42	0.074	23.83	1.60	-0.120
0.88	0.12	13.68	7.25	99.18	1.99	4.59	0.046	24.65	4.00	-0.185
0.94	0.06	15.40	7.45	114.7	2.05	4.74	0.023	25.50	5.00	-0.115

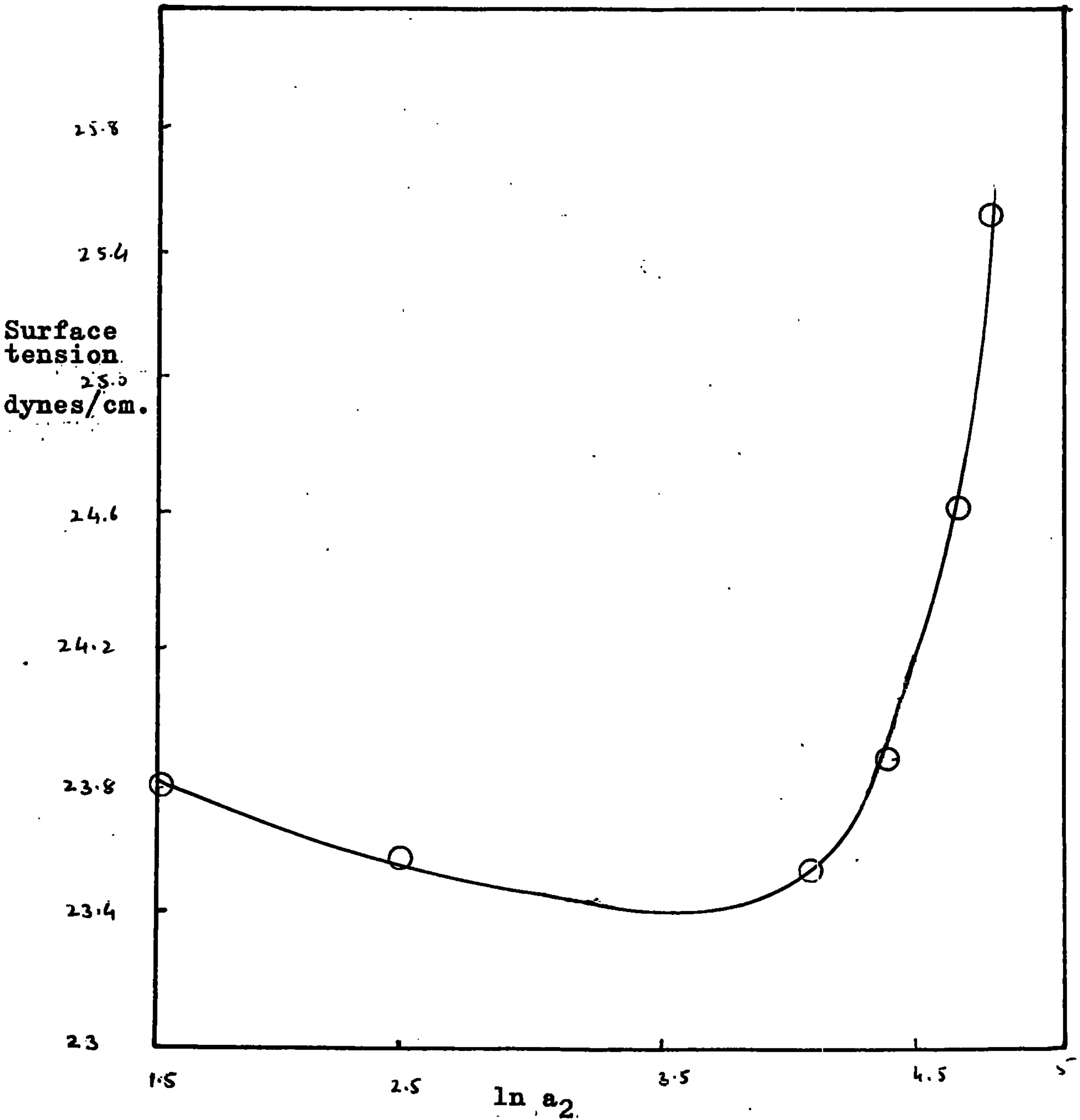

Fig.20-Plot of ln a_2 against surface tension of acetic acid + cyclohexane system at 30° C.

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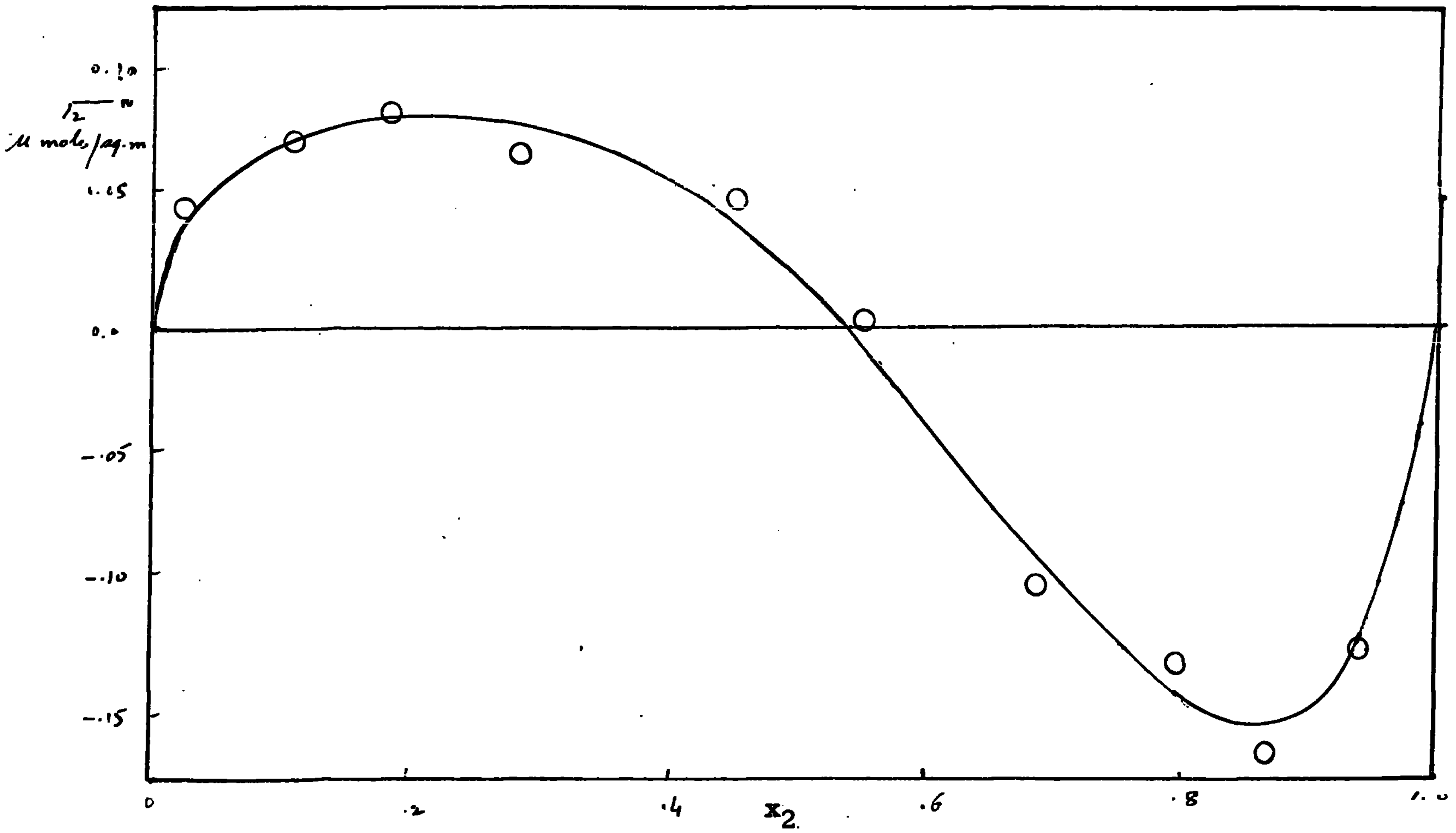


Fig.21- Composite isotherm showing surface excess in acetic acid + cyclohexane system at the solution-vapour interface.

TABLE 46.

Surface excess in acetic acid + ethyl alcohol system.

x_2	x_1	m_2	f_2	a_2	log a_2	ln a_2	$\frac{x_1}{RT}$ $\times 10^{-10}$	γ Dynes/cm	$-\frac{d\gamma}{d\ln a_2}$	Γ_2^N μ moles/sq.m.
0.06	0.94	1.00	1.000	1.01	0.02	0.04	0.374	21.80	0.285	-0.140
0.12	0.88	2.08	1.019	2.12	0.32	0.75	0.348	22.06	0.625	-0.220
0.22	0.78	3.82	1.027	3.93	0.59	1.36	0.308	22.85	1.454	-0.445
0.34	0.66	5.85	1.033	6.04	0.78	1.79	0.262	23.51	1.700	-0.445
0.44	0.56	7.65	1.037	7.94	0.90	2.07	0.221	23.95	2.000	-0.442
0.55	0.45	9.55	1.038	9.92	0.99	2.30	0.179	24.54	2.380	-0.426
0.65	0.35	11.25	1.039	11.69	1.06	2.46	0.140	24.91	2.860	-0.400
0.80	0.20	13.83	1.404	14.39	1.16	2.66	0.081	25.50	3.330	-0.268

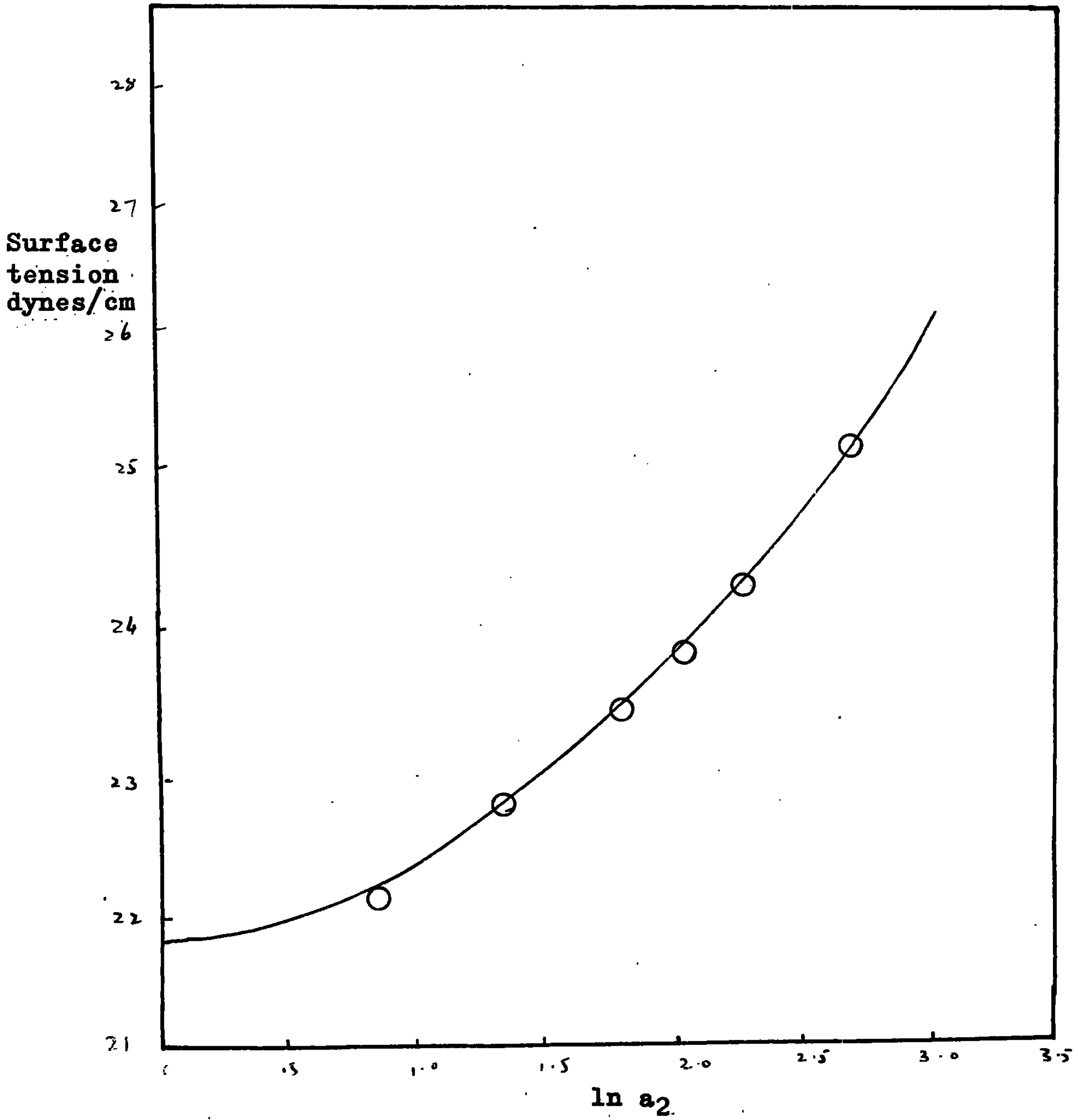


Fig.22– Plot of ln a_2 against surface tension of acetic acid + ethanol system at 30°C.

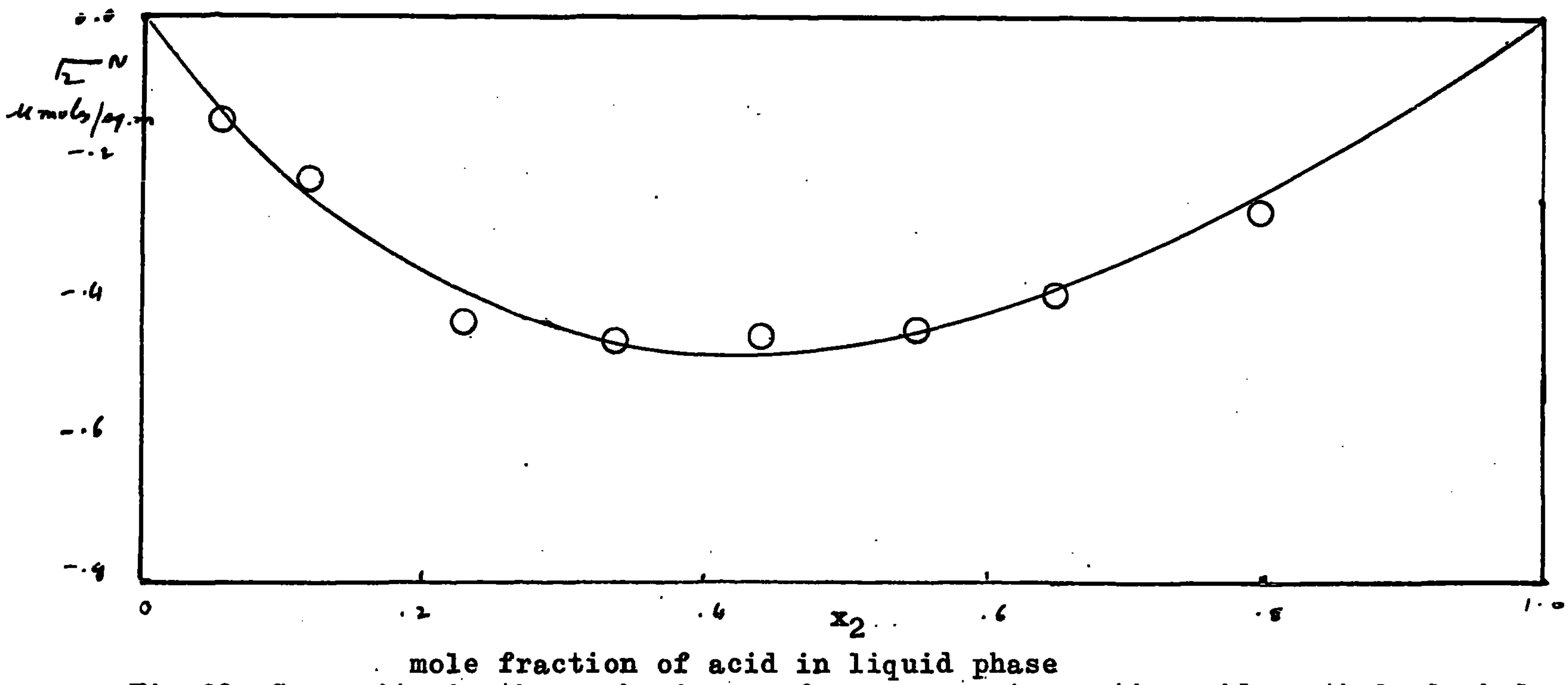


Fig.23- Composite isotherm showing surface excess in acetic acid + ethyl alcohol system at the solution-vapour interface.

TABLE 47.

Surface excess in acetic acid + water system.

x_2	x_1	m_2	f_2	a_2	log a_2	ln a_2	$\frac{x_1}{RT}$	γ Dynes/cm	$\frac{d\gamma}{d\ln a_2}$	Γ_2^N μ moles/sq.m.
0.03	0.97	1.6	1.026	1.69	0.23	0.53	0.384×10^{-10}	55.45	9.43	3.630
0.05	0.95	2.4	1.028	2.46	0.39	0.90	0.378	50.70	10.00	3.780
0.09	0.91	4.4	1.032	4.49	0.65	1.50	0.360	44.96	10.00	3.600
0.13	0.87	5.9	1.035	6.13	0.78	1.81	0.344	42.41	10.21	3.510
0.22	0.78	8.5	1.040	8.84	0.94	2.18	0.310	38.40	10.71	3.300
0.35	0.65	11.1	1.043	11.59	1.06	2.45	0.258	36.95	10.91	2.810
0.51	0.49	13.7	1.047	14.39	1.16	2.66	0.193	33.37	11.50	2.210
0.69	0.31	15.5	1.050	16.27	1.21	2.78	0.123	31.00	12.66	1.562
0.85	0.15	16.6	1.053	17.47	1.24	2.86	0.059	29.50	13.80	0.779

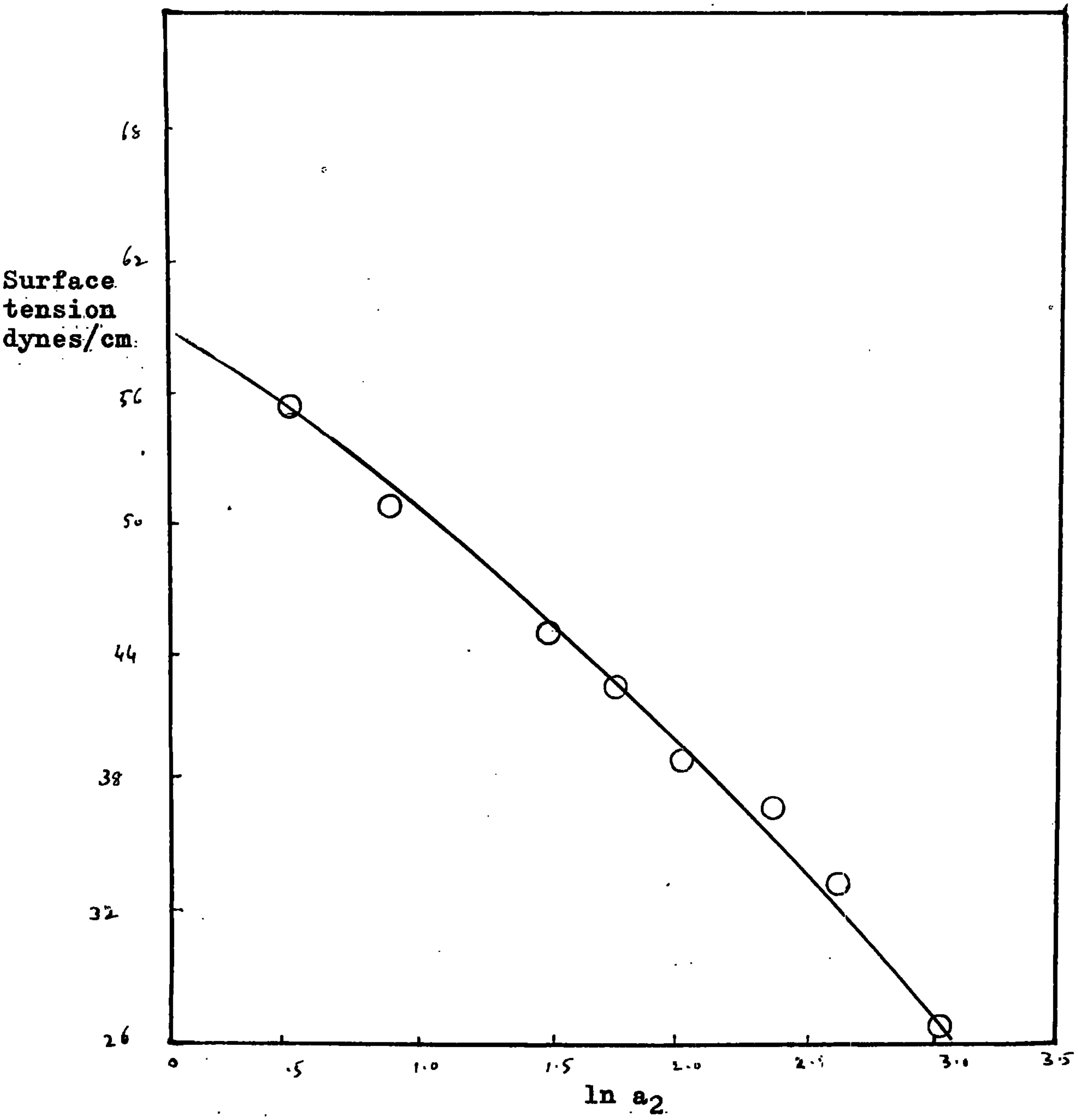


Fig.24– Plot of ln a_2 against surface tension of acetic acid + water system at 30° C.

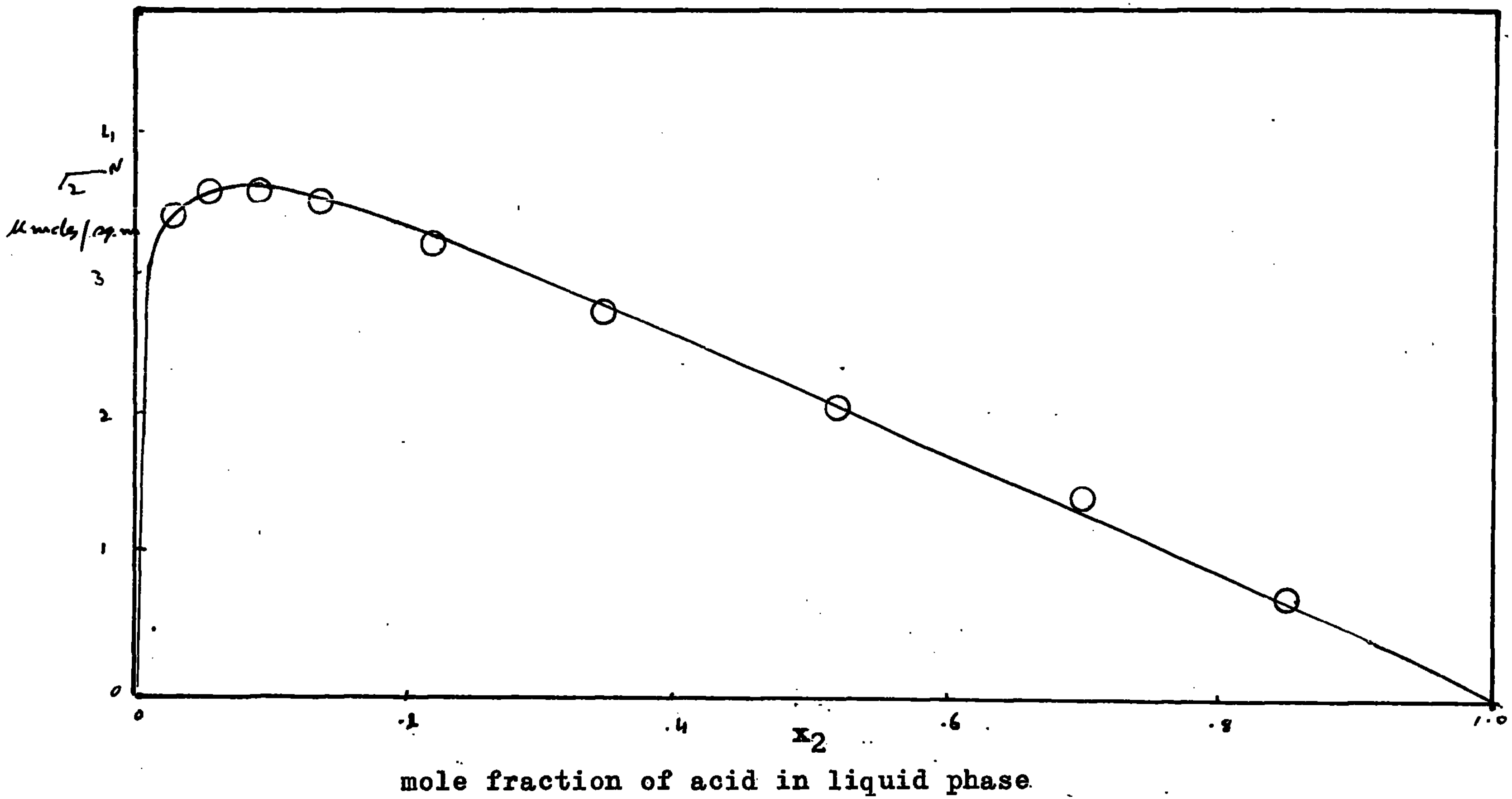


Fig.25- Composite isotherm showing surface excess in acetic acid + water system at the solution-vapour interface.

TABLE 48.

Surface excess in propionic acid + benzene system.

x_2	x_1	m_2	f_2	a_2	log a_2	ln a_2	$\frac{-x_1}{RT}$ 10^{-10} ×10	γ Dynes/cm	$\frac{d\gamma}{d\ln a_2}$	Γ^{N} µ moles/sq.m.
0.09	0.91	1.91	1.08	2.07	0.31	0.73	0.360	27.26	0.40	0.180
0.15	0.85	2.96	1.12	3.31	0.52	1.20	0.339	27.07	0.50	0.169
0.26	0.74	4.89	1.18	5.77	0.76	1.75	0.294	26.86	0.625	0.184
0.39	0.61	6.84	1.23	8.44	0.92	2.13	0.242	26.69	0.933	0.226
0.47	0.53	7.95	1.27	10.09	1.04	2.39	0.209	26.50	0.966	0.202
0.58	0.42	9.20	1.30	11.98	1.08	2.48	0.167	26.34	1.066	0.178
0.72	0.28	10.76	1.33	14.36	1.15	2.66	0.200	26.13	1.20	0.132
0.86	0.14	12.01	1.36	16.34	1.21	2.79	0.057	25.90	1.33	0.076

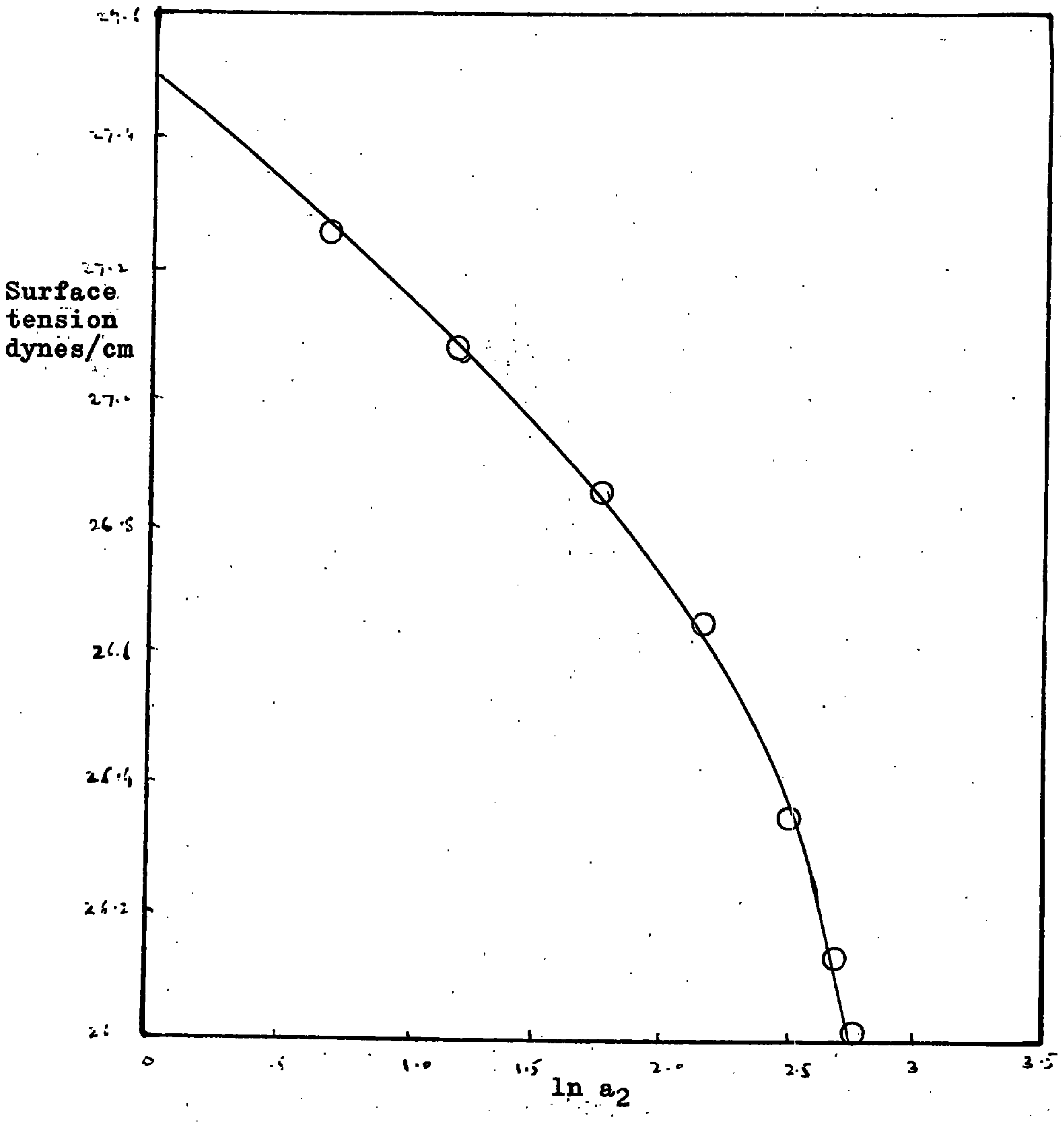


Fig.26- Plot of ln a_2 against surface tension of propionic acid + benzene system at 30°C.

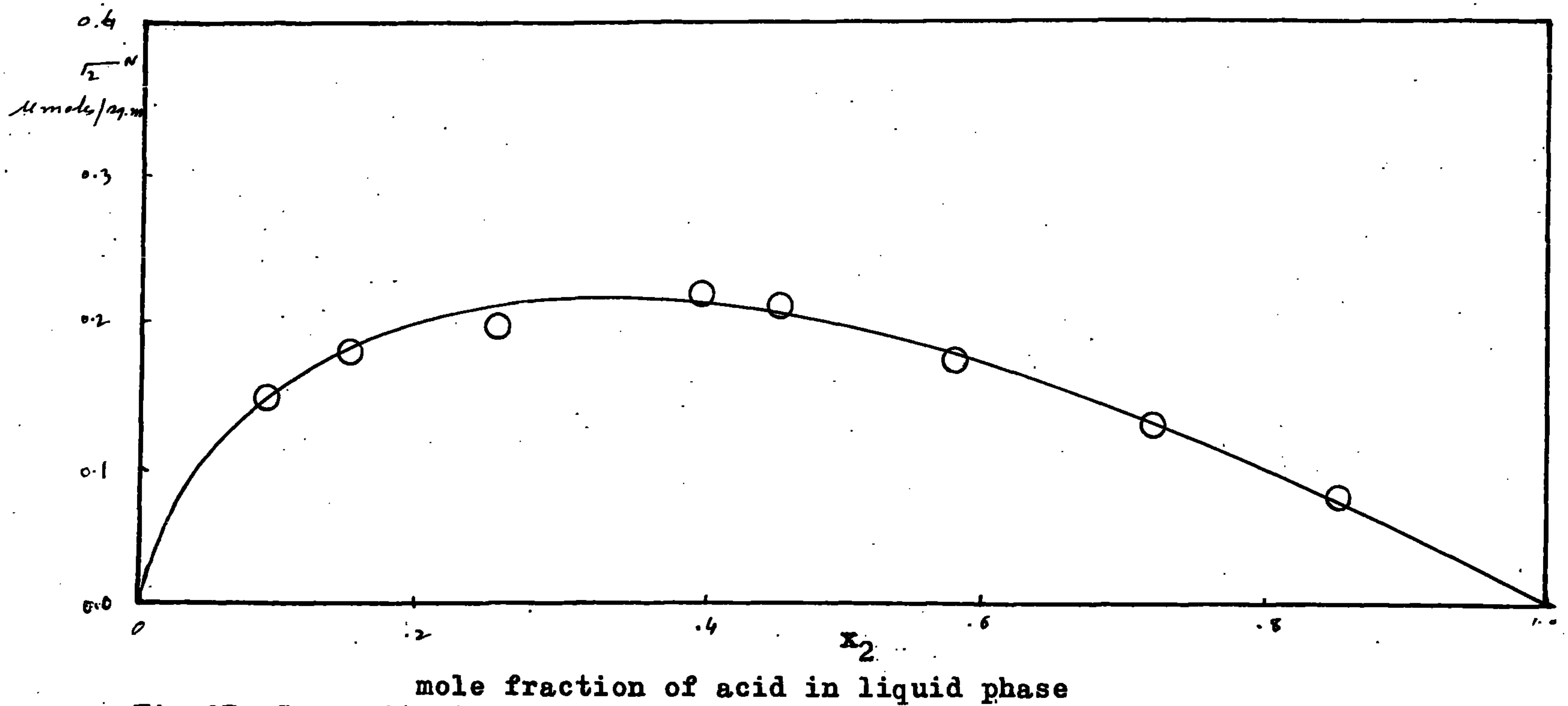


Fig.27- Composite isotherm showing surface excess in propionic acid + benzene system at solution-vapour interface.

TABLE 49.

Surface excess in propionic acid + carbon tetrachloride system.

x_2	x_1	m_2	f_2	a_2	log a_2	ln a_2	$\frac{-x_1}{RT} \times 10^{-10}$	γ_{30}	$\frac{d\gamma}{d \ln a_2}$	Γ_2^{N} μ moles/sq.m.
0.08	0.92	1.63	1.13	1.85	0.27	0.61	0.364	25.46	0.330	+0.115
0.19	0.81	3.47	1.21	4.22	0.62	1.44	0.322	25.37	0.240	+0.077
0.31	0.69	5.34	1.31	6.98	0.84	1.94	0.275	25.29	0.192	+0.053
0.41	0.59	6.92	1.38	9.55	0.98	2.25	0.232	25.18	0.125	-0.030
0.57	0.43	8.87	1.47	13.09	1.11	2.56	0.171	25.29	0.400	-0.075
0.73	0.27	10.66	1.56	16.62	1.22	2.81	0.108	25.39	0.571	-0.062
0.91	0.09	12.31	1.64	20.17	1.30	3.00	0.038	25.58	0.800	-0.032

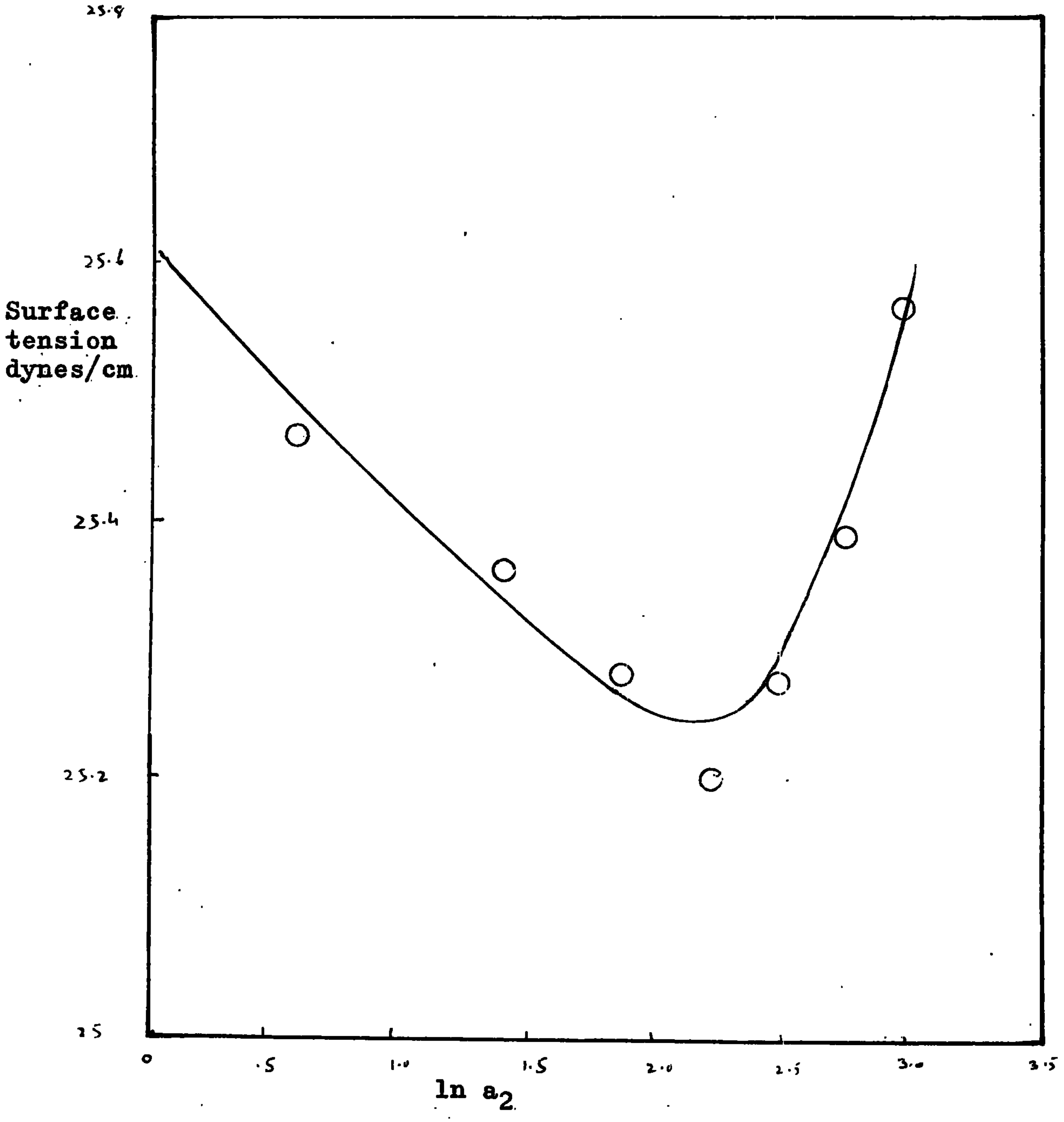
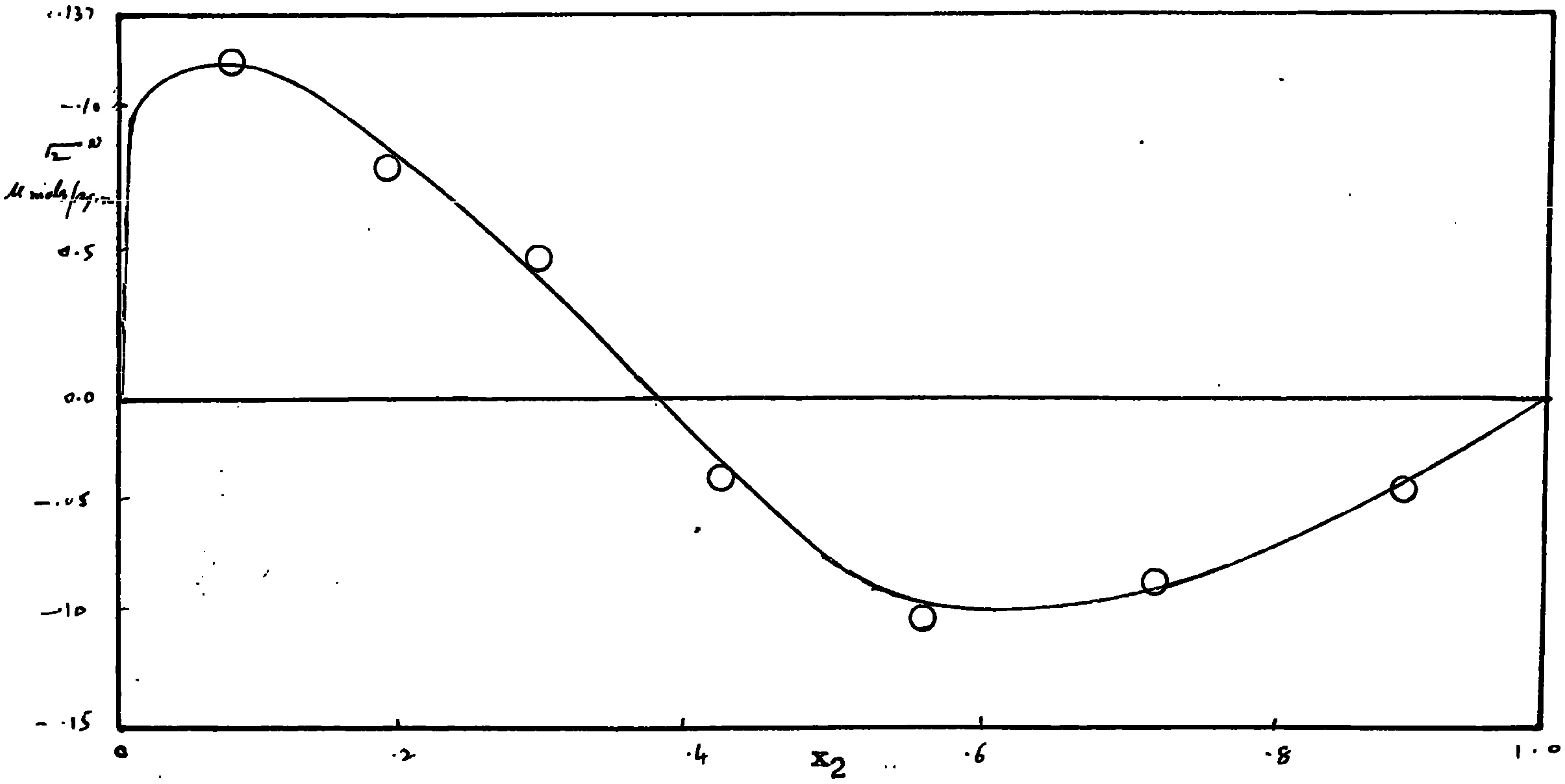


Fig.28- Plot of ln a_2 against surface tension of propionic acid + carbon tetrachloride system at 30°C.



mole fraction of acid in liquid phase
Fig.29- Composite isotherm showing surface excess in propionic acid + carbon tetrachloride system at solution-vapour interface.

TABLE 50.

Surface excess in propionic acid + cyclohexane system.

x_2	x_1	m_2	f_2	a_2	$\log a_2$	$\ln a_2$	$\frac{-x_1}{RT} \times 10^{-10}$	γ Dynes/cm	$\frac{d\gamma}{d\ln a_2}$	Γ_2^N μ moles/sq.m.
0.09	0.91	0.67	1.50	1.605	0.002	0.18	0.392	24.04	0.07	-0.027
0.21	0.79	2.01	2.94	5.900	0.771	1.77	0.315	24.13	0.10	-0.032
0.38	0.62	3.88	4.00	15.520	1.191	2.74	0.247	24.23	0.291	-0.072
0.53	0.47	5.94	4.70	27.940	1.446	3.33	0.187	24.45	0.545	-0.102
0.69	0.31	7.92	5.30	41.900	1.623	3.73	0.124	24.66	0.840	-0.104
0.82	0.18	9.95	5.70	56.700	1.754	4.03	0.072	25.00	1.200	-0.087
0.91	0.09	11.5	5.88	67.500	1.830	4.21	0.037	25.21	1.867	-0.069

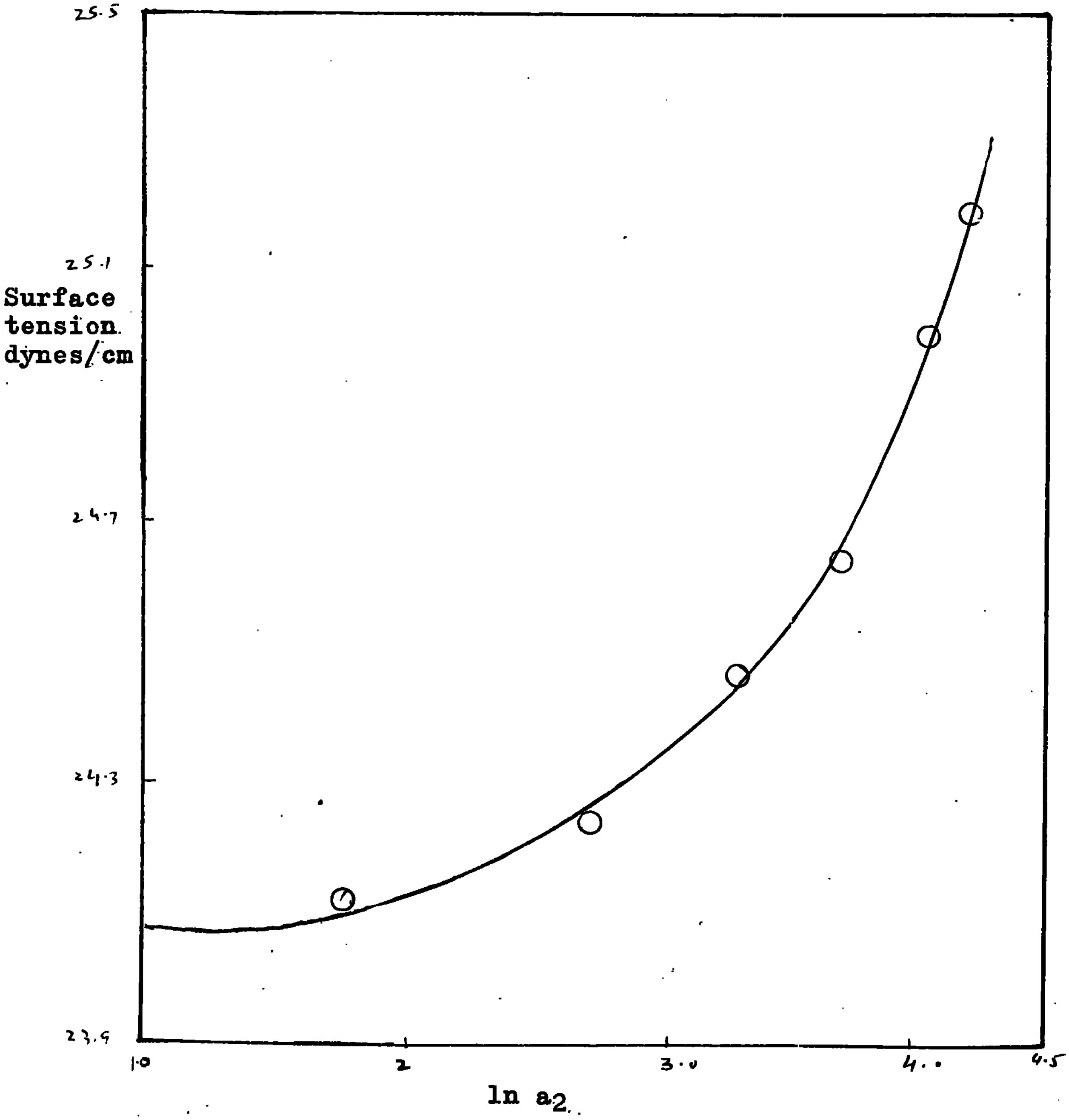


Fig.30- Plot of ln a_2 against surface tension of propionic acid + cyclohexane system at 30° C.

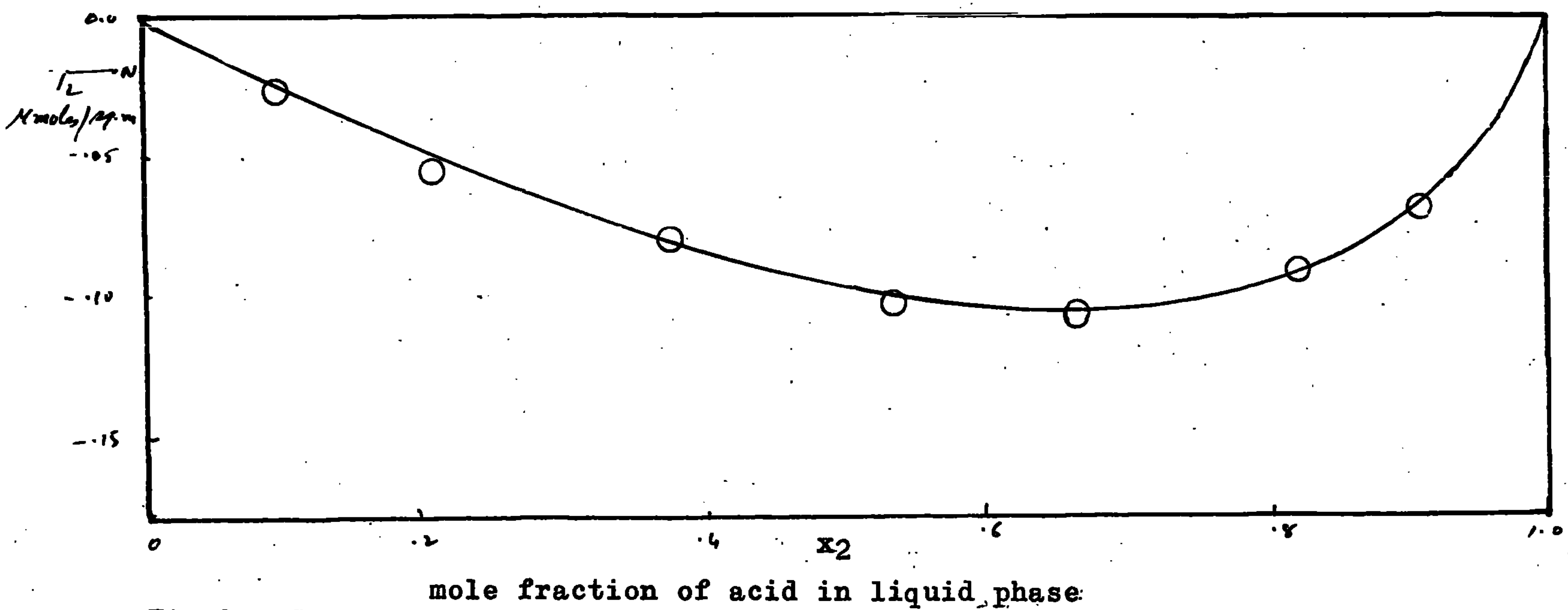


Fig.31– Composite isotherm showing surface excess in propionic acid + cyclohexane system at solution–vapour interface.

TABLE 51.

Surface excess in propionic acid + ethyl alcohol system.

x_2	x_1	m_2	f_2	a_2	log a_2	ln a_2	$\frac{-x_1}{RT}$ $\times 10^{-10}$	γ Dynes/cm	$\frac{d\gamma}{d\ln a_2}$	Γ_2^N μ moles/sq.m.
0.06	0.94	1.01	1.007	1.02	0.008	0.020	0.372	21.60	0.400	-0.140
0.10	0.90	1.62	1.010	1.63	0.210	0.490	0.358	22.00	0.666	-0.238
0.14	0.86	2.35	1.013	2.38	0.38	0.860	0.340	22.24	1.00	-0.340
0.22	0.78	3.57	1.019	3.64	0.56	1.29	0.309	22.15	1.538	-0.475
0.32	0.68	4.99	1.023	5.11	0.71	1.63	0.271	23.15	1.818	-0.493
0.43	0.57	6.57	1.028	6.75	0.83	1.91	0.227	23.67	2.000	-0.453
0.57	0.43	8.41	1.030	8.66	0.93	2.15	0.171	24.26	2.222	-0.381
0.75	0.25	10.67	1.030	10.99	1.04	2.39	0.097	25.00	2.222	-0.216
0.87	0.13	12.02	1.031	12.39	1.09	2.51	0.052	25.50	2.400	-0.124

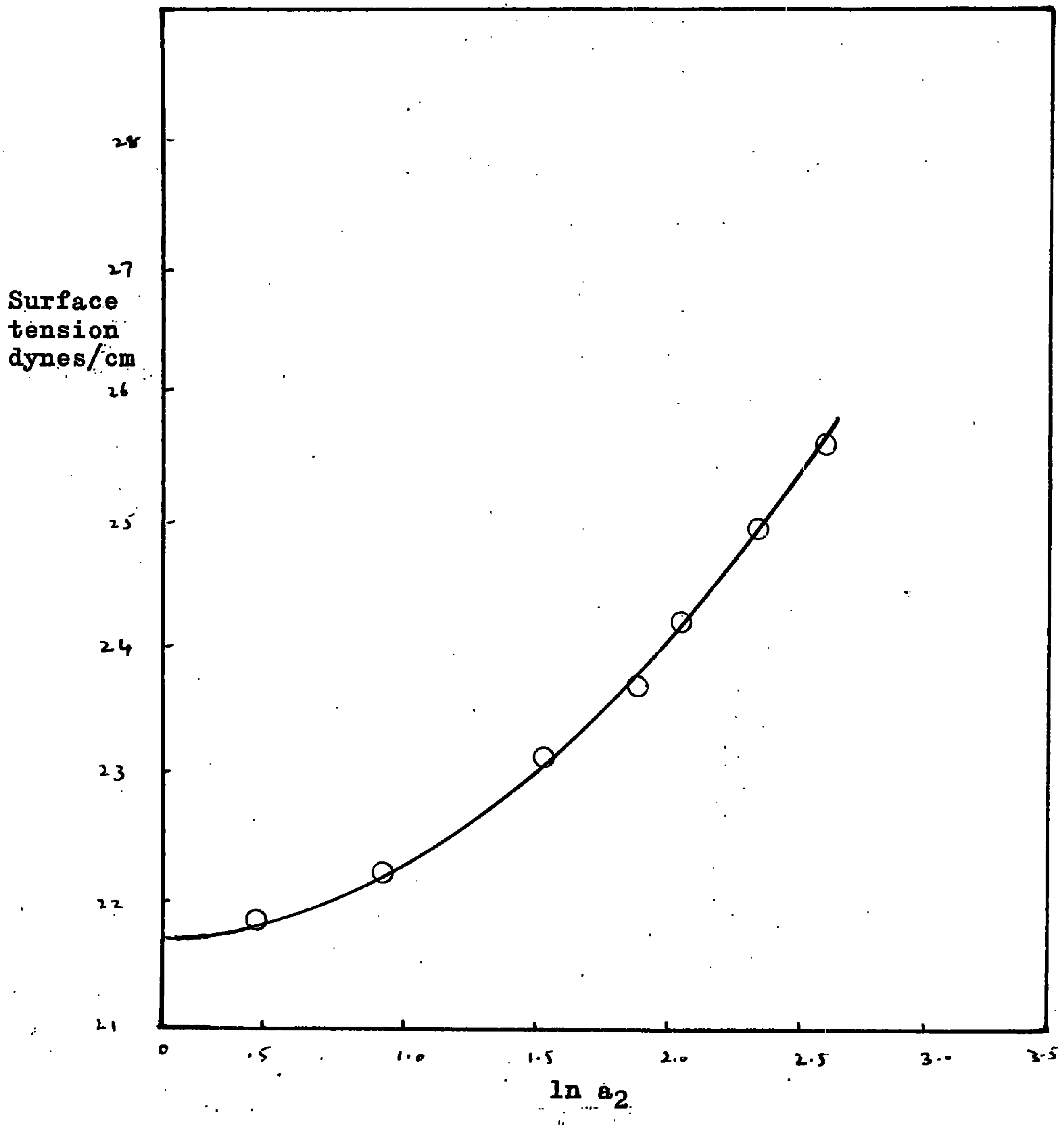


Fig.32- Plot of ln a_2 against surface tension of propionic acid + ethanol system at 30° C.

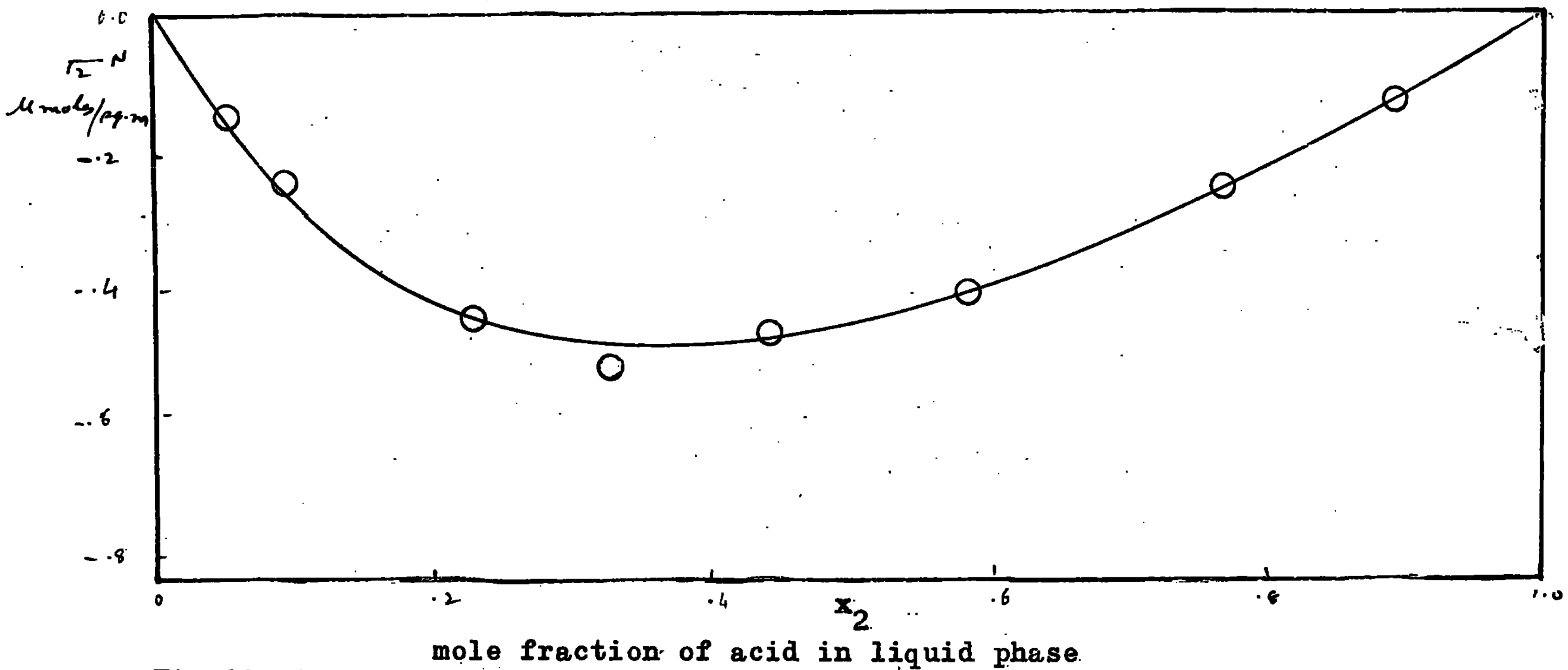


Fig.33- Composite isotherm showing surface excess in propionic acid + ethanol system at solution-vapour interface.

TABLE 52.

Surface excess in propionic acid + water system.

x_2	x_1	m_2	f_2	a_2	log a_2	ln a_2	$\frac{-x_1}{RT}$ $\times 10^{-10}$	γ Dynes/cm	$\frac{\partial \gamma}{d\ln a_2}$	Γ^{N} μ moles/sq.m.
0.02	0.98	0.92	1.09	1.01	0.004	0.008	0.390	50.00	11.00	4.288
0.06	0.94	2.76	1.10	3.05	0.484	1.116	0.374	42.00	11.04	4.125
0.09	0.91	3.98	1.11	4.41	0.645	1.484	0.361	38.10	10.76	3.886
0.12	0.88	5.06	1.12	5.64	0.751	1.730	0.347	36.60	10.80	3.752
0.17	0.83	6.42	1.13	7.24	0.859	1.980	0.327	34.00	10.80	3.531
0.25	0.75	7.88	1.15	9.03	0.955	2.200	0.299	32.00	10.90	3.260
0.31	0.69	8.89	1.16	10.33	1.014	2.330	0.274	31.06	11.11	3.045
0.44	0.56	10.43	1.19	12.46	1.095	2.520	0.223	28.96	11.40	2.540
0.60	0.40	11.68	1.23	14.42	1.159	2.660	0.159	27.35	12.00	1.905
0.85	0.15	13.00	1.50	16.50	1.200	2.810	0.059	27.00	13.00	0.080

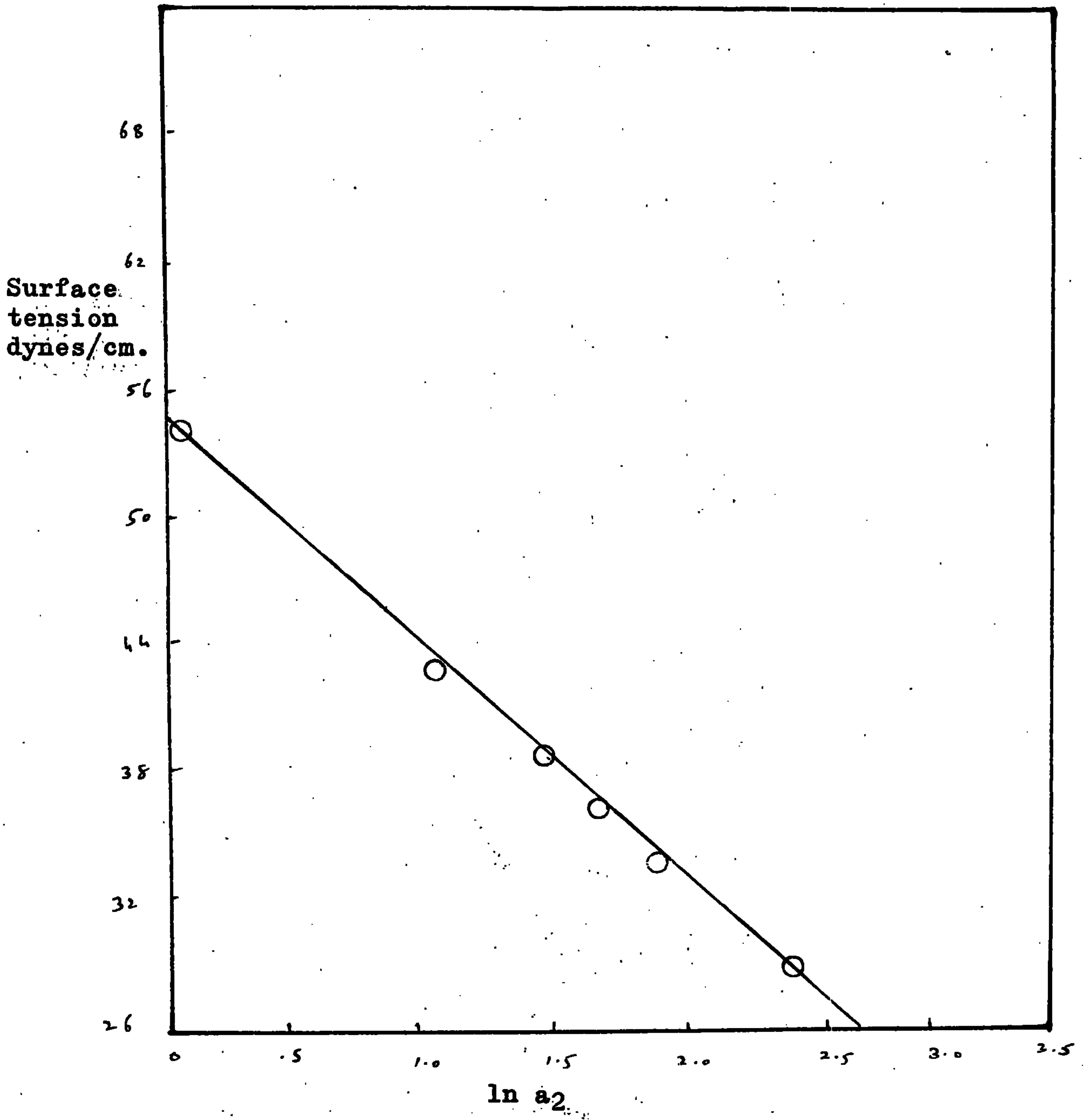


Fig.34- Plot of ln a_2 against surface tension of propionic acid + water system at 30°C.

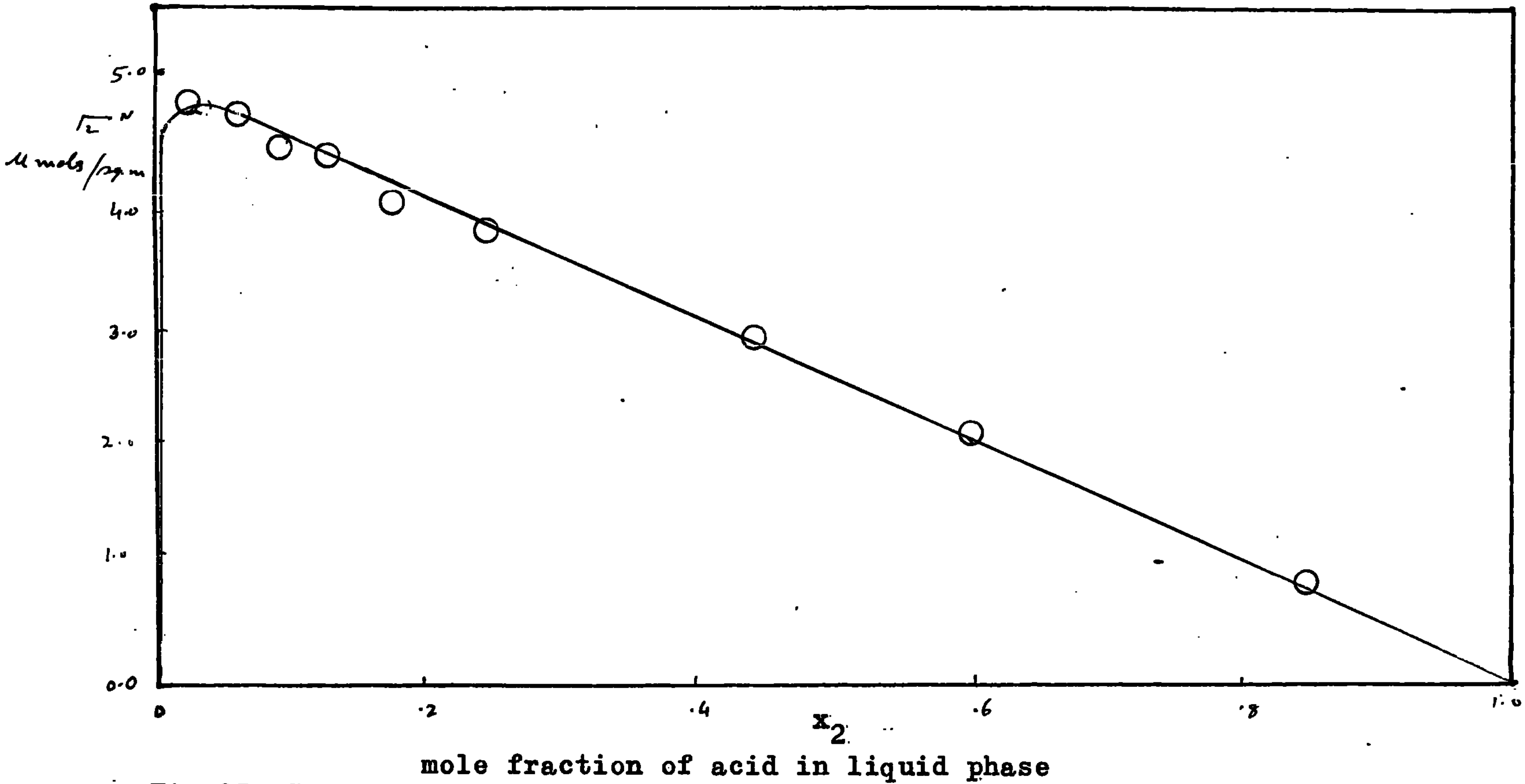


Fig.35- Composite isotherm showing surface excess in propionic acid + water system at solution-vapour interface.

TABLE 53.

Surface excess in butyric acid + benzene system.

x_2	x_1	m_2	f_2	a_2	log a_2	ln a_2	$\frac{-x_1}{RT} \times 10^{-10}$	γ Dynes/cm	$\frac{d\gamma}{d\ln a_2}$	$\Gamma^{\sim}$ μ moles/sq.m.
0.07	0.93	1.42	1.044	1.48	0.171	0.393	0.370	27.22	0.480	0.177
0.12	0.88	2.41	1.060	2.55	0.407	0.937	0.348	26.97	0.225	0.216
0.19	0.81	3.50	1.077	3.77	0.576	1.327	0.322	26.75	0.809	0.257
0.30	0.70	5.14	1.093	5.61	0.749	1.725	0.276	26.50	0.840	0.232
0.35	0.65	6.02	1.100	6.62	0.821	1.890	0.258	26.30	0.900	0.232
0.49	0.51	7.15	1.112	7.95	0.900	2.073	0.202	26.12	1.070	0.216
0.61	0.39	8.19	1.120	9.18	0.962	2.217	0.155	25.97	1.200	0.186
0.82	0.18	9.77	1.128	11.02	1.042	2.399	0.069	25.73	1.490	0.103.

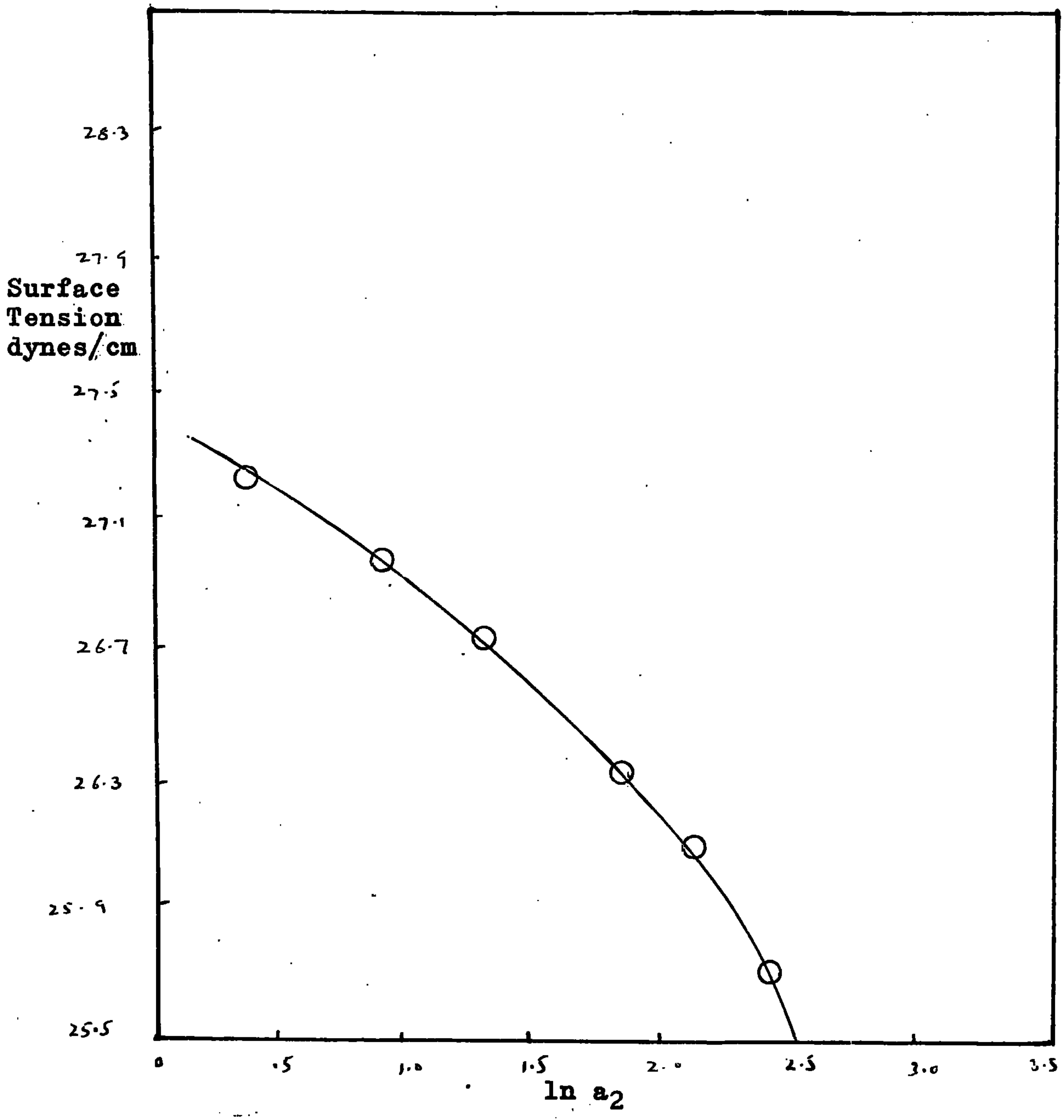


Fig.36- Plot of ln a_2 against surface tension of butyric acid + benzene system at 30°C.

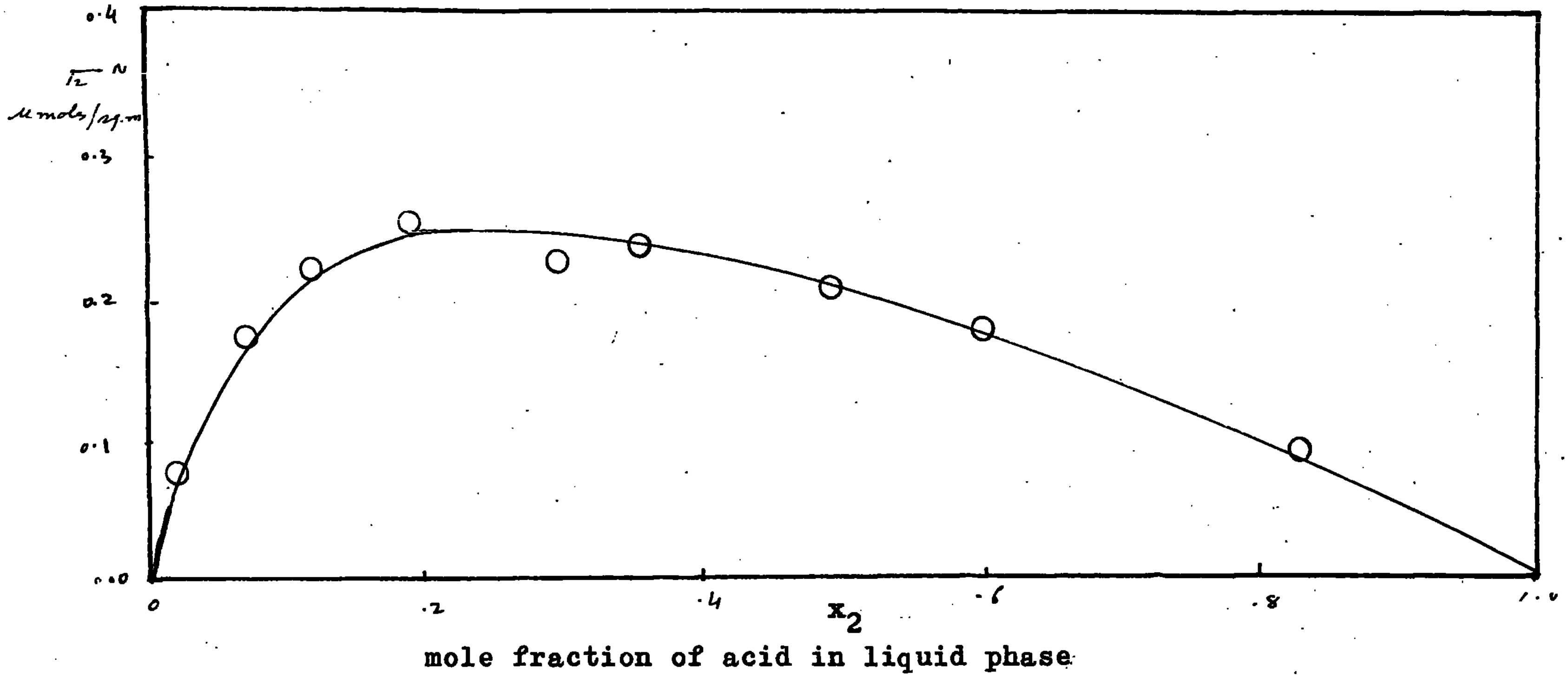


Fig.37- Composite isotherm showing surface excess in butyric acid + benzene system at solution-vapour interface.

TABLE 54.

Surface excess in butyric acid + carbon tetrachloride system.

x_2	x_1	m_2	f_2	a_2	log a_2	ln a_2	$\frac{-x_1}{RT}$ $\times 10^{-10}$	γ Dynes/cm	$\frac{d\gamma}{d\ln a_2}$	Γ_2^N μ moles/sq.m.
0.06	0.94	1.19	1.09	1.29	0.112	0.258	0.373	25.47	0.406	0.151
0.14	0.86	2.54	1.13	2.88	0.460	1.058	0.341	25.36	0.370	0.126
0.22	0.78	3.84	1.16	4.46	0.668	1.540	0.307	25.27	0.230	0.070
0.31	0.69	4.99	1.18	5.90	0.770	1.760	0.273	25.20	0.226	0.060
0.45	0.55	6.34	1.20	7.64	0.883	2.033	0.218	25.27	0.327	-0.071
0.60	0.40	8.05	1.21	9.78	0.990	2.280	0.158	25.39	0.325	-0.051
0.79	0.21	7.48	1.22	11.61	1.065	2.450	0.081	25.44	0.366	-0.029

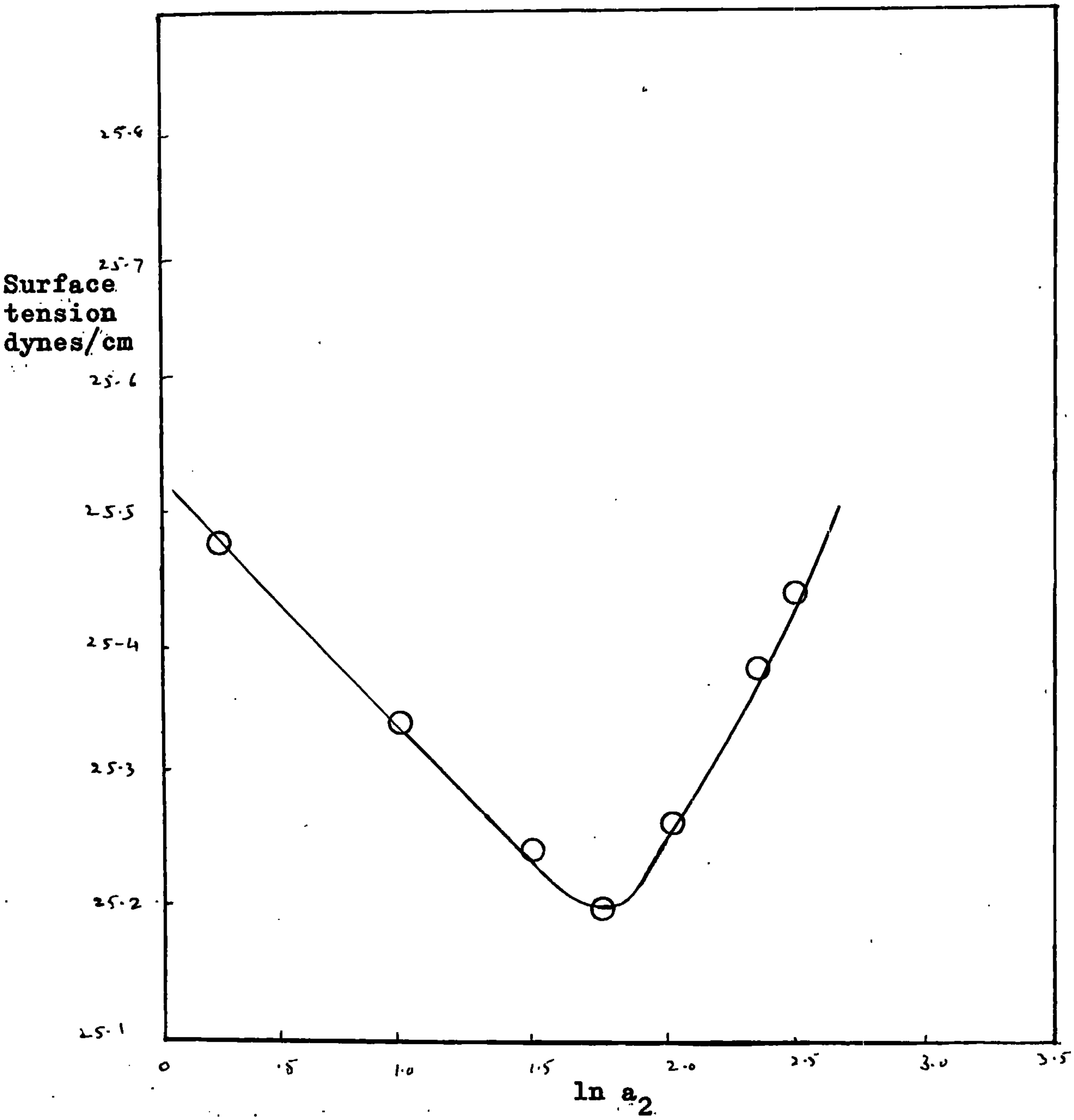


Fig.38– Plot of ln a_2 against surface tension of butyric acid + carbon tetrachloride system at 30° C.

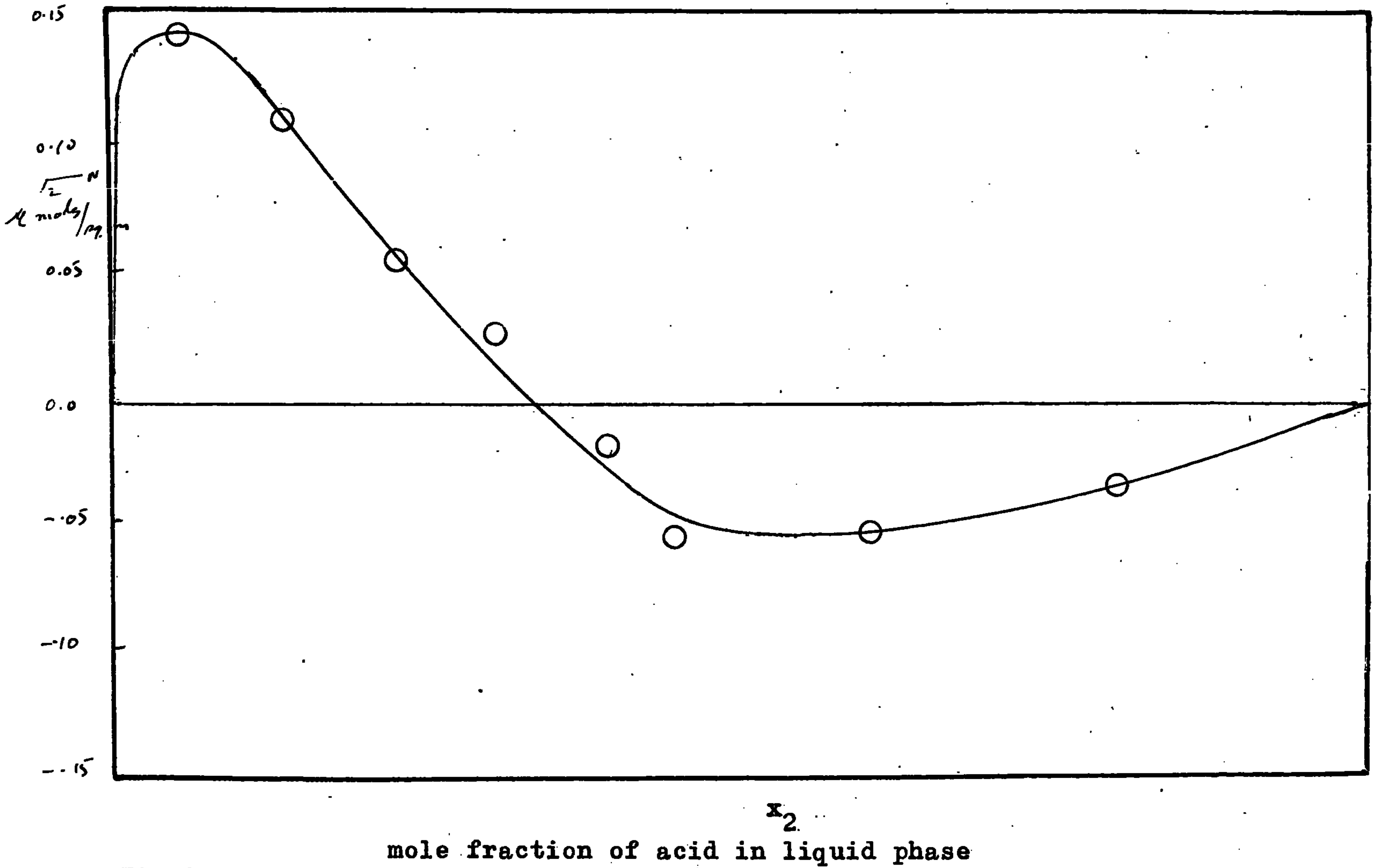


Fig.39- Composite isotherm showing surface excess in butyric acid + carbon tetrachloride system at solution-vapour interface.

TABLE 55.

Surface excess in butyric acid + cyclohexane system.

x_2	x_1	m_2	f_2	a_2	log a_2,	ln a_2	$\frac{-x_1}{RT}$ $\times 10^{-10}$	γ Dynes/cm	$\frac{d\gamma}{d\ln a_2}$	Γ_2^N μ moles/sq.m.
0.10	0.90	0.10	1.800	1.76	0.244	0.563	0.355	24.00	0.120	-0.042
0.19	0.81	1.73	2.45	4.25	0.629	1.448	0.320	24.23	0.200	-0.065
0.31	0.69	2.97	3.15	9.36	0.971	2.237	0.273	24.36	0.266	-0.073
0.40	0.60	4.03	3.50	14.11	1.149	2.647	0.238	24.59	0.364	-0.087
0.59	0.41	5.82	4.15	24.15	1.383	3.185	0.164	24.68	0.545	-0.090
0.68	0.32	6.93	4.40	30.50	1.484	3.417	0.125	24.81	0.850	-0.107
0.79	0.21	8.25	4.55	37.50	1.574	3.627	0.081	25.03	1.314	-0.108
0.90	0.10	9.33	4.65	43.40	1.637	3.771	0.044	25.26	1.250	-0.055

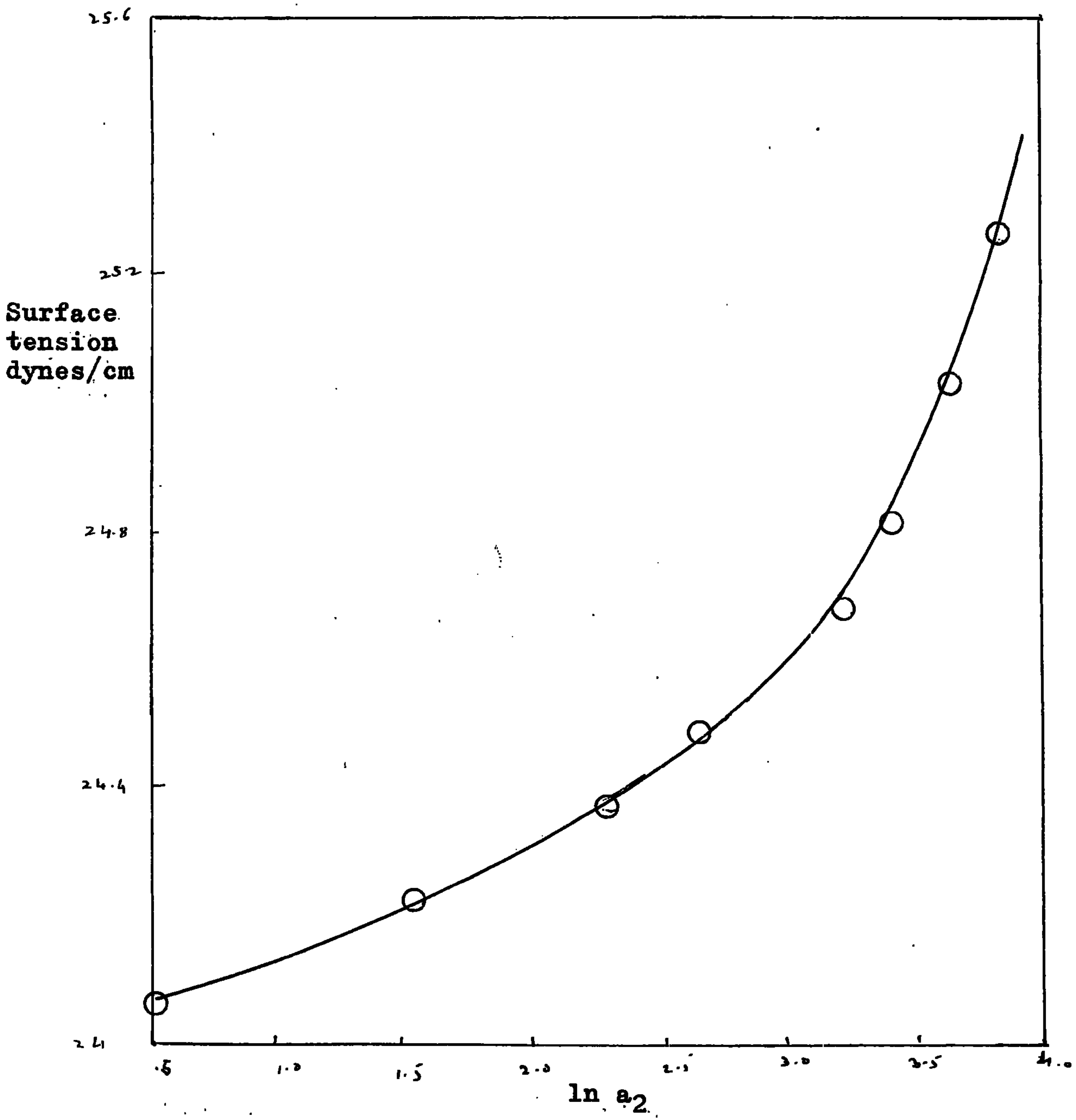


Fig.40- Plot of ln a_1 against surface tension of butyric acid + cyclohexane system at 30° C.

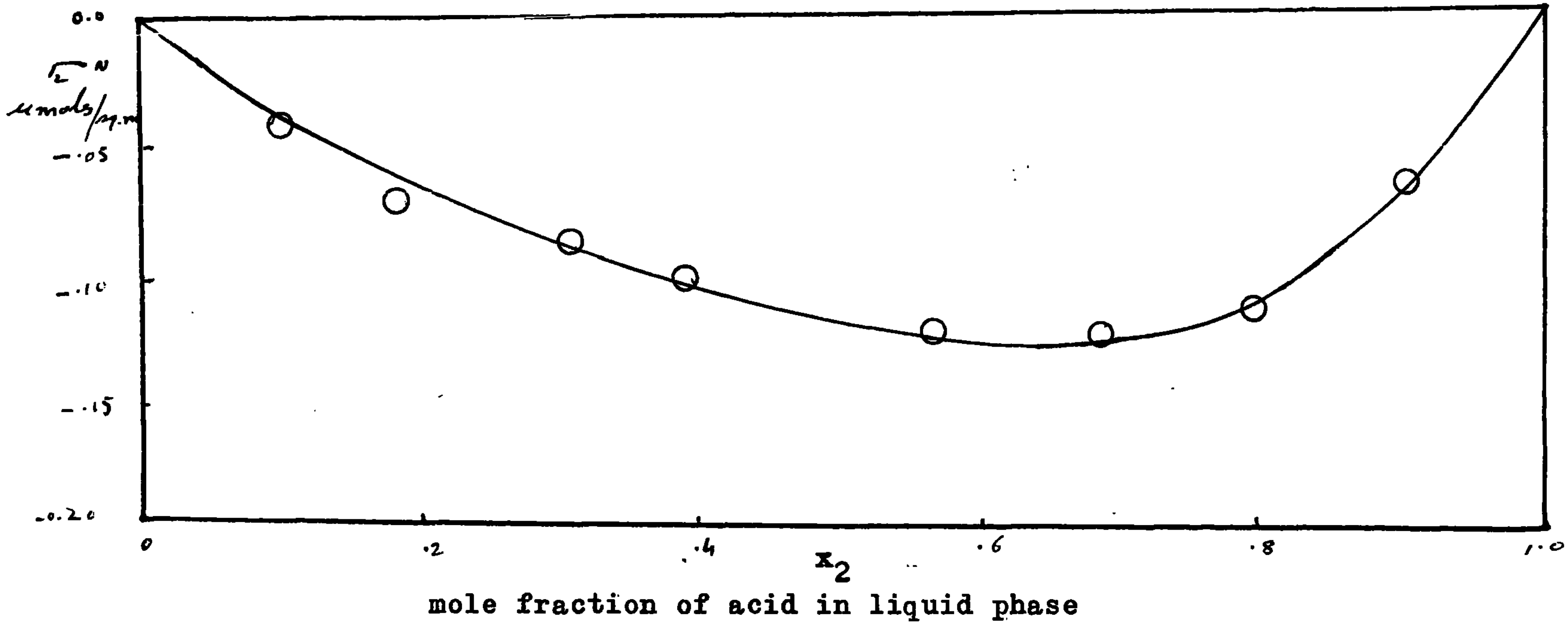


Fig.41– Composite isotherm showing surface excess in butyric acid + cyclohexane system at solution-vapour interface.

TABLE 56.

Surface excess in butyric acid + water system.

x_2	x_1	m_2	f_2	a_2	$\log a_2$	$\ln a_2$	$\frac{-x_1}{RT} \times 10^{-10}$	γ Dynes/cm	$\frac{d\gamma}{d\ln a_2}$	Γ^{N} μ moles/sq.m.
0.02	0.98	1.16	1.09	1.26	0.102	0.236	0.388	44.10	12.00	4.653
0.07	0.93	2.94	1.28	3.76	0.575	1.325	0.370	37.80	11.55	4.277
0.13	0.87	4.67	1.44	6.11	0.826	1.903	0.347	34.10	11.11	3.850
0.22	0.78	6.53	1.72	11.24	1.051	2.419	0.309	31.80	10.00	3.085
0.28	0.72	7.31	1.85	13.53	1.131	2.605	0.286	30.00	9.00	2.570
0.40	0.60	8.52	2.05	17.46	1.240	2.861	0.237	28.00	7.50	1.776
0.65	0.35	9.86	2.25	22.26	1.346	3.100	0.140	26.28	4.00	0.556
0.85	0.15	10.44	2.35	24.22	1.384	3.200	0.057	25.82	2.00	0.114

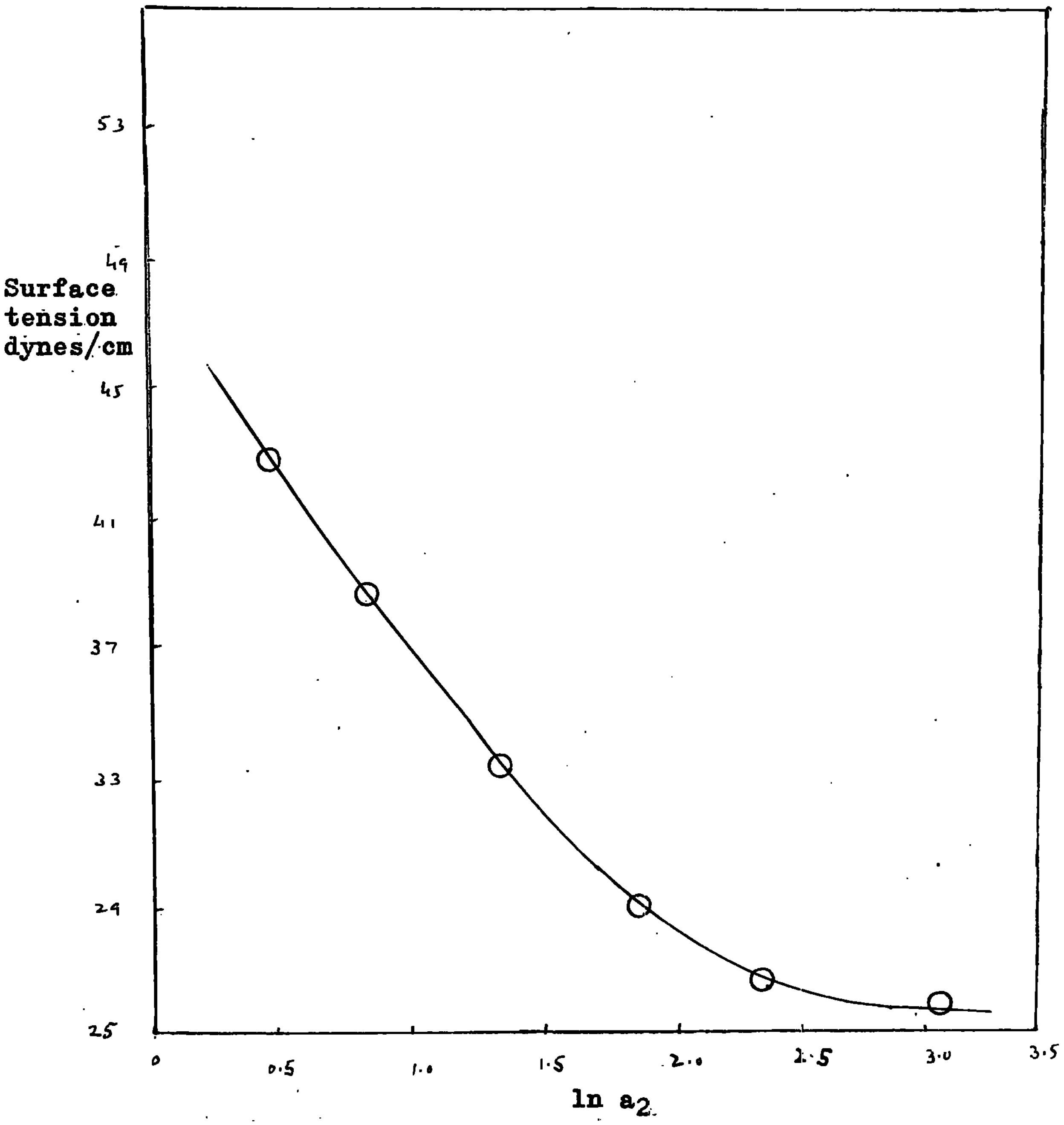
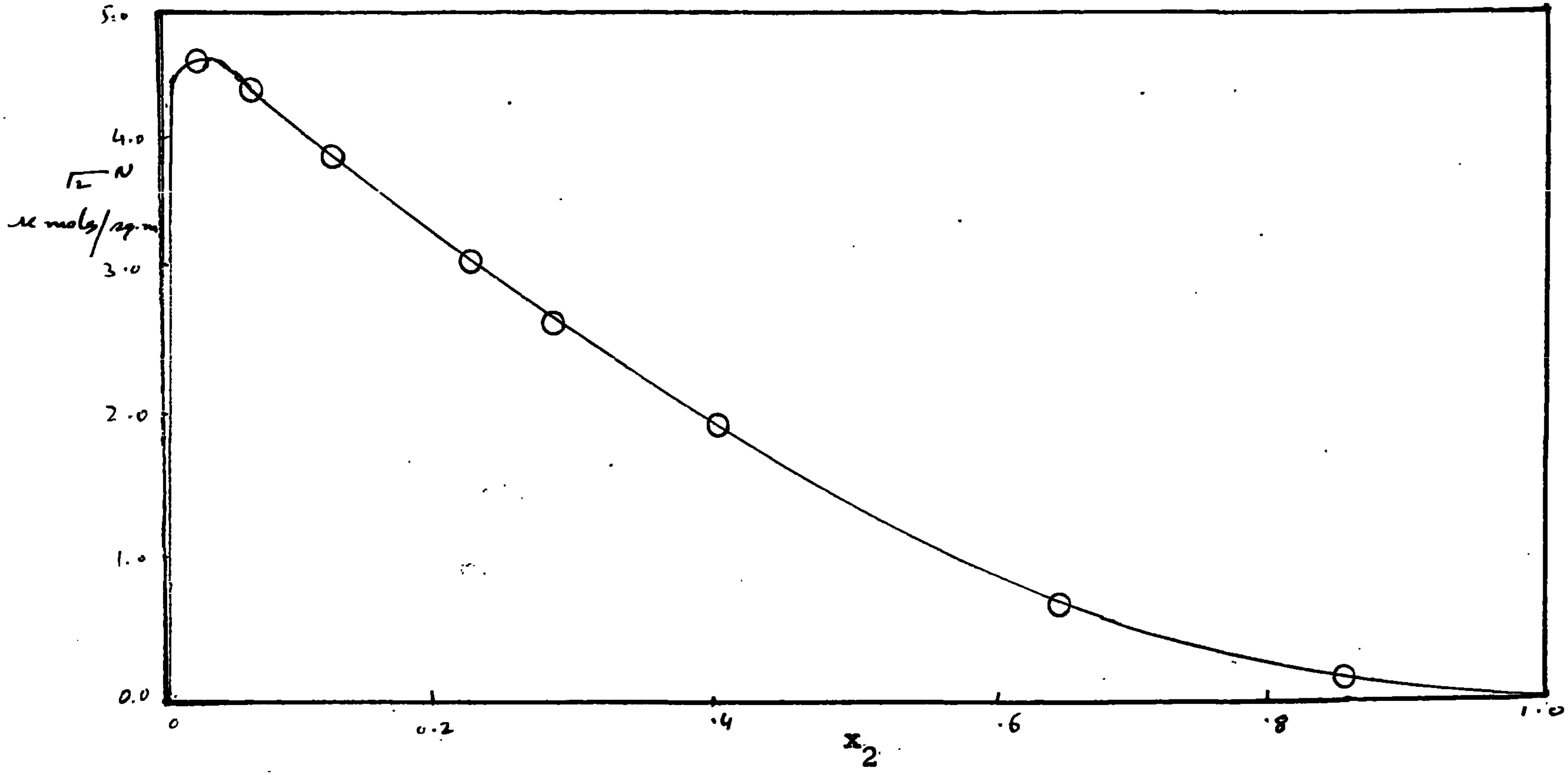


Fig.42- Plot of ln a_2 against surface tension of butyric acid + water system at 30°C.



mole fraction of acid in liquid phase

Fig.43- Composite isotherm showing surface excess in butyric acid + water system at solution-vapour interface.

TABLE 57.

Number of moles of different components required to form a complete monolayer.

Component	Orientation	Area Sq.A	No. of Moles for monolayer $(\Gamma_{\parallel}^{s})_m$ or $(\Gamma_{\perp}^{s})_m$	
Acetic acid	Parallel perpendicular	28.1 25.8	5.91 6.43	μ moles/sq.m.
Propionic acid	Parallel perpendicular	33.1 20.5	5.02 8.11	"
Butyric acid	Parallel perpendicular	38.0 20.5	4.37 8.11	"
Benzene	Parallel	43.0	3.86	"
Carbon tet.	-	45.0	3.69	"
Cyclohexane	Parallel	48.0	3.46	"
Ethanol	Perpendicular	21.5	7.75	"
Water	-	10.0	16.60	"

TABLE 58.

Amounts of the individual components at the interface for the acetic acid + benzene system.
Solvent and solute molecules oriented parallel to surface.

M.F. of acid x_2	M.F. of benz. x_1	Surface excess Γ_2^N	Γ_2^s acid	Γ_1^s benzene	
0.05	0.95	+0.10	0.29	3.70	μ moles/sq.m.
0.10	0.90	+0.15	0.52	3.42	"
0.20	0.80	+0.20	1.00	3.16	"
0.30	0.70	+0.18	1.21	2.88	"
0.45	0.55	+0.12	2.20	2.42	"
0.60	0.40	-0.04	2.87	1.98	"
0.70	0.30	-0.13	3.39	1.64	"
0.80	0.20	-0.10	4.13	1.16	"
0.90	0.10	-0.06	4.95	0.62	"
0.95	0.05	-0.003	5.41	0.29	"

TABLE 59.

Amounts of the individual components at the interface for the acetic acid + CCl_4 system.

Solvent and solute molecules oriented parallel to surface.

M.F. of acid x_2	M.F. of CCl_4 x_1	Surface excess	acid Γ_2^s	CCl_4 Γ_1^s	
0.05	0.95	+0.095	0.28	3.51	μ moles/sq.m.
0.10	0.90	+0.100	0.48	3.38	"
0.20	0.80	+0.100	0.90	3.13	"
0.30	0.70	+0.050	1.30	2.88	"
0.45	0.55	-0.140	1.83	2.55	"
0.60	0.40	-0.195	2.61	2.06	"
0.70	0.30	-0.160	3.28	1.64	"
0.80	0.20	-0.120	4.05	1.16	"
0.90	0.10	-0.07	4.91	0.83	"

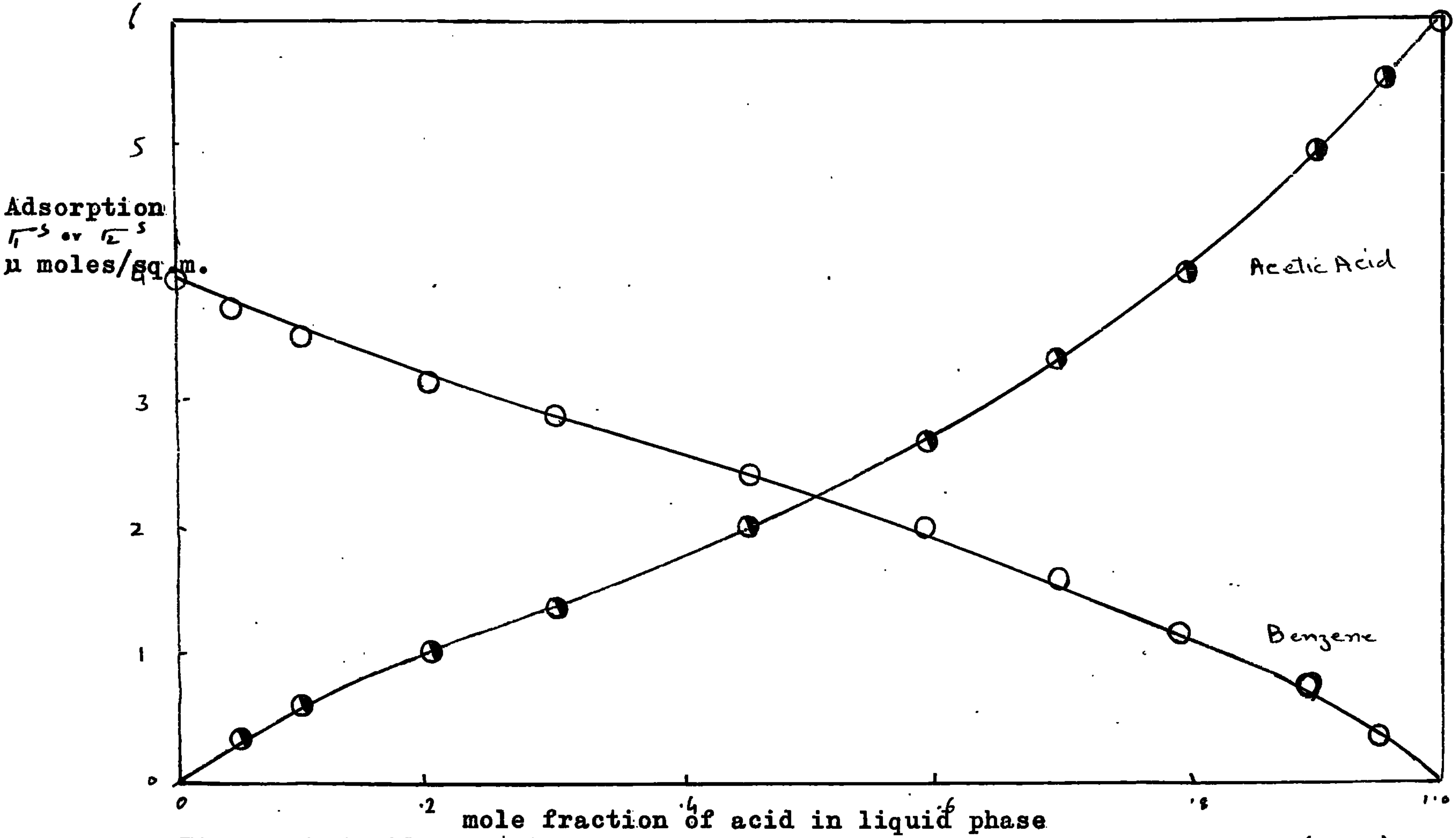


Fig.44- Individual isotherms for adsorption of acetic acid and benzene (30 C) with the major axes of both molecules parallel to the surface.

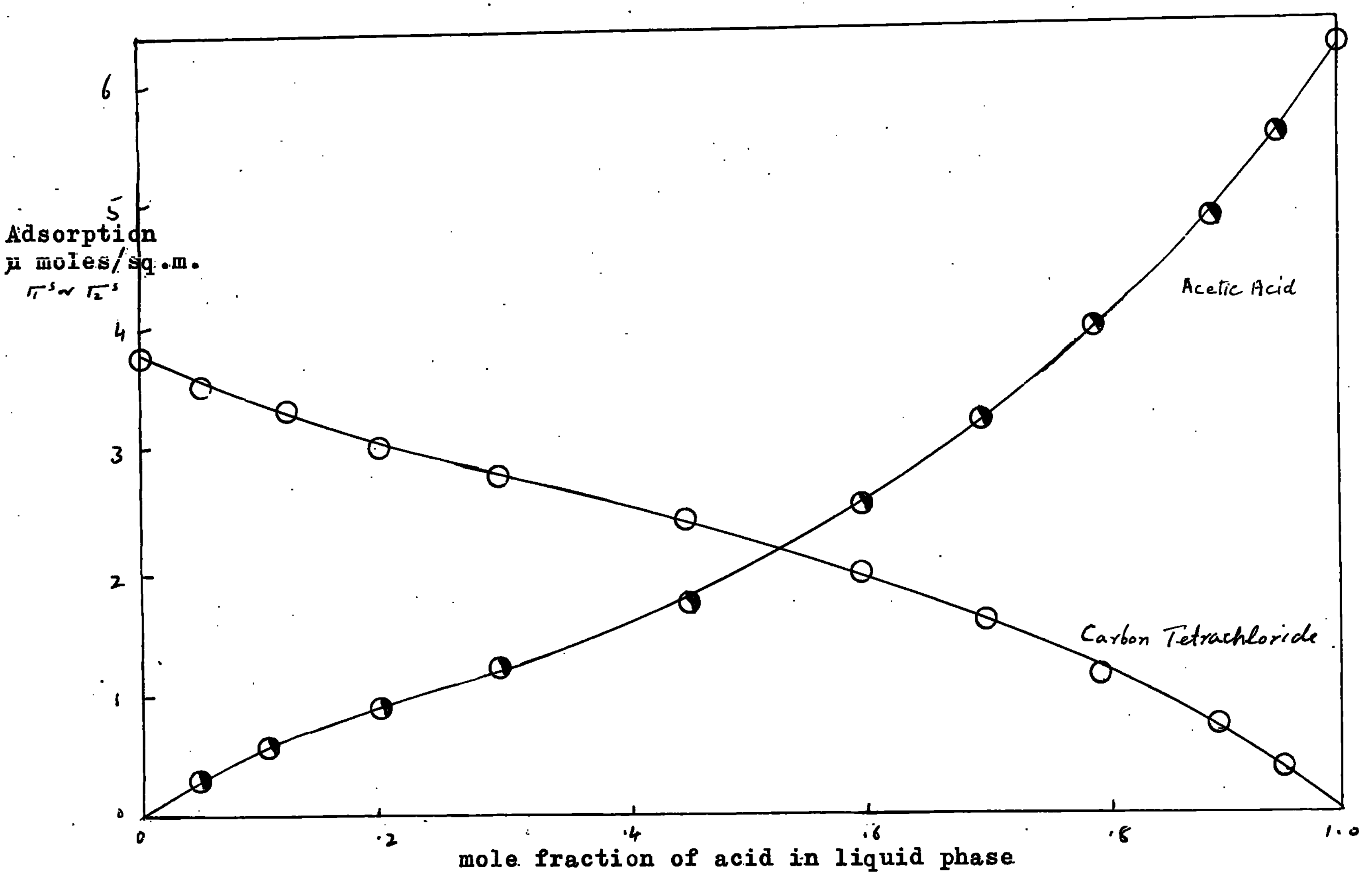


Fig.45- Individual isotherms for adsorption of acetic acid and carbon tetrachloride with the major axes of both molecules parallel to the surface.

TABLE 60.

Amounts of the individual components at the interface for the cyclohexane system.
Solvent and solute molecules oriented parallel to surface.

M.F. of acid x_2	M.F. of cycl. x_1	surface excess	Γ_2^s acid	Γ_1^s cyclohexane	
0.05	0.95	+0.060	0.24	3.32	μ moles/sq.m.
0.10	0.90	+0.075	0.46	3.20	"
0.20	0.80	+0.080	0.75	2.97	"
0.45	0.55	+0.045	1.97	2.31	"
0.60	0.40	-0.037	2.71	1.87	"
0.70	0.30	-0.092	3.28	1.54	"
0.80	0.20	-0.145	3.92	1.16	"
0.95	0.05	-0.125	5.20	0.41	"

TABLE 61.

Amounts of the individual components at the interface for the ethanol system.
Solvent and solute molecules oriented perpendicularly.

M.F. of acid x_2	M.F. of eth. x_1	surface excess	Γ_2^s acid	Γ_1^s ethanol	
0.05	0.95	-0.13	0.24	7.27	μ moles/sq.m.
0.10	0.90	-0.23	0.50	6.94	"
0.20	0.80	-0.37	1.11	6.22	"
0.30	0.70	-0.48	1.72	5.40	"
0.45	0.55	-0.48	2.67	4.20	"
0.60	0.40	-0.43	3.82	3.26	"
0.70	0.30	-0.36	4.39	2.39	"
0.80	0.20	-0.25	5.08	1.58	"
0.90	0.10	-0.13	5.76	0.78	"
0.95	0.05	-0.07	6.10	0.39	"

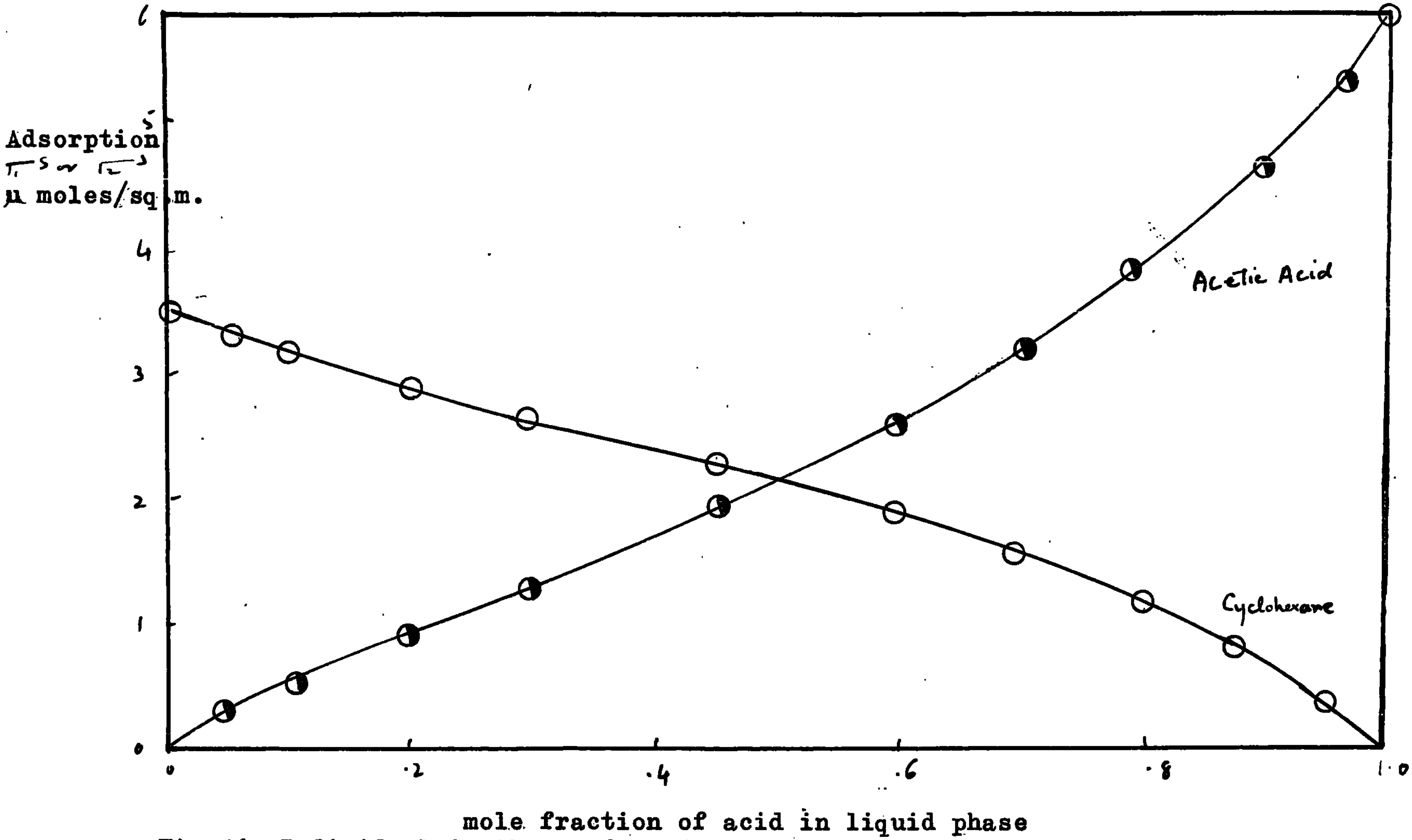


Fig.46– Individual isotherms for adsorption of acetic acid and cyclohexane with the major axes of both molecules parallel to the surface.

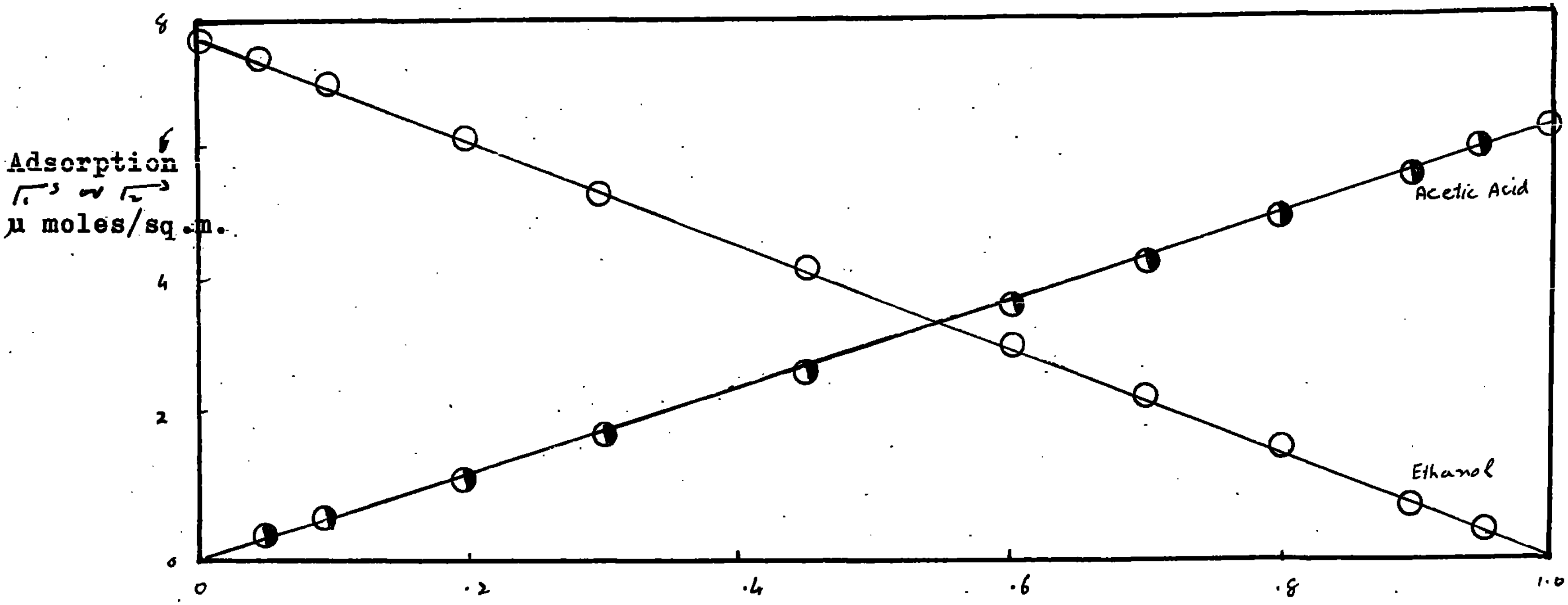


Fig.47- Individual isotherms for adsorption of acetic acid and ethyl alcohol with the major axes of both molecules perpenducular to the surface.

TABLE 62.

Amounts of the individual components at the interface for the water system.
Solvent and solute molecules oriented perpendicularly.

M.F. of acid x_2	M.F. of water x_1	Surface excess	Γ_2^s acid	Γ_1^s water	
0.05	0.95	3.70	4.20	5.78	µ moles/sq.m.
0.10	0.90	3.60	4.54	4.90	"
0.20	0.80	3.30	5.03	3.63	"
0.30	0.70	2.95	5.38	2.72	"
0.45	0.55	2.40	5.77	1.71	"
0.60	0.40	1.80	6.03	1.02	"
0.70	0.30	1.40	6.18	0.65	"
0.80	0.20	1.00	6.31	0.33	"
0.90	0.10	0.50	6.38	0.15	"

TABLE 63.

Amounts of the individual components at the interface for the propionic acid + benzene system.
Solvent and solute molecules oriented parallel to surface.

M.F. of acid x_2	M.F. of benz. x_1	Surface excess	Γ_2^s acid	Γ_1^s benzene	
0.05	0.95	0.21	0.31	3.73	µ moles/sq.m.
0.10	0.90	0.18	0.58	3.41	"
0.20	0.80	0.20	1.02	3.07	"
0.30	0.70	0.23	1.47	2.67	"
0.50	0.50	0.20	2.41	2.00	"
0.70	0.30	0.14	3.39	1.25	"
0.80	0.20	0.09	3.89	0.86	"
0.90	0.10	0.04	4.43	0.45	"
0.95	0.05	0.01	4.68	0.23	"

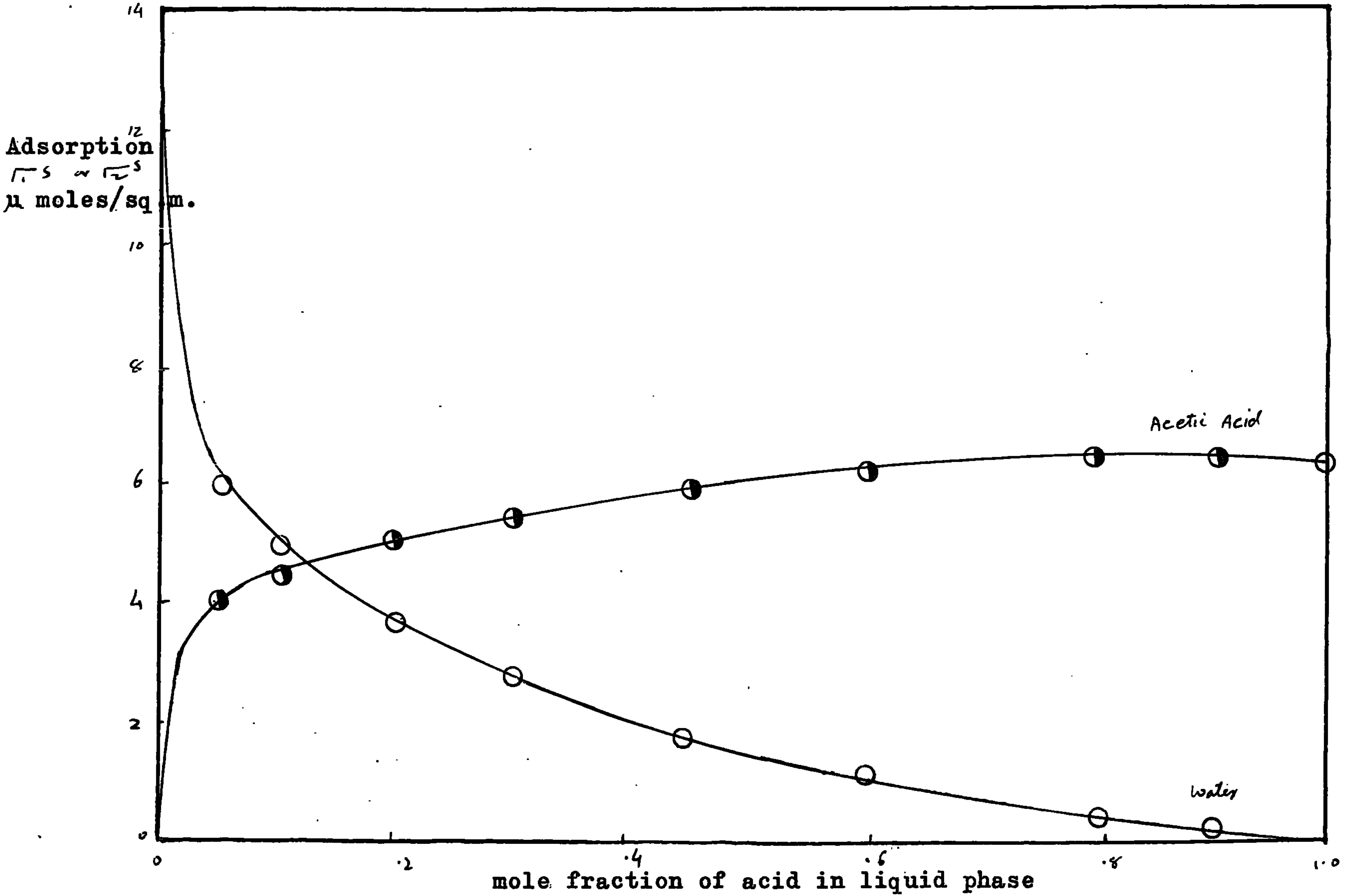


Fig.48- Individual isotherms for adsorption of acetic acid and water with the major axes of both molecules perpendicular to the surface.

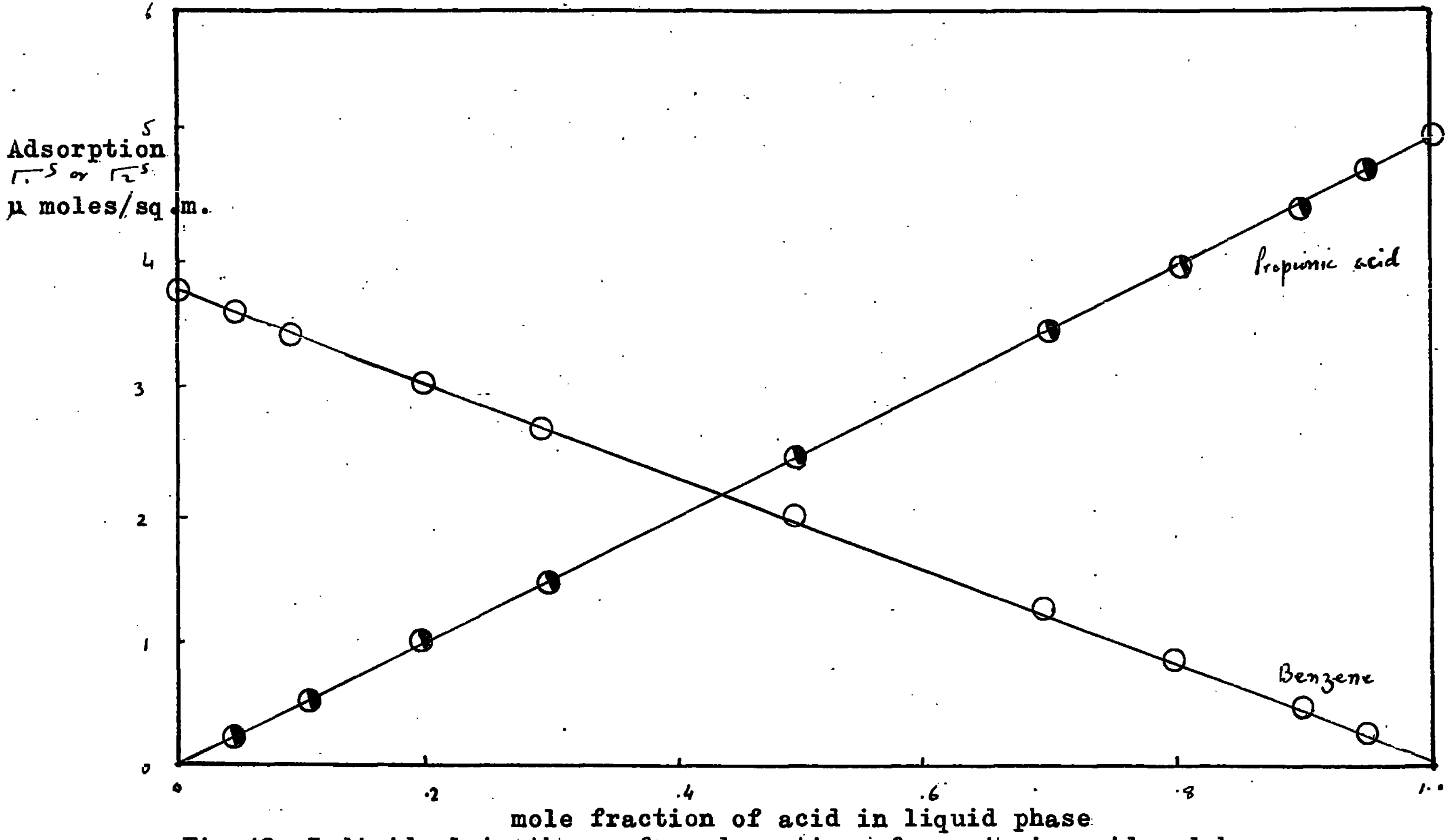


Fig.49– Individual isotherms for adsorption of propionic acid and benzene with major axes of both molecules parallel to the surface.

TABLE 64.

Amounts of the individual components at the interface for the propionic acid + carbon tetrachloride system.

Solvent and solute molecules oriented parallel to surface.

M.F. of acid x_2	M.F. of CCl$_4$ x_1	Surface excess	Γ_2^s acid	Γ_1^s carbon	tetrachloride
0.05	0.95	0.120	0.31	3.46	μ moles/sq.m.
0.10	0.90	0.110	0.49	3.33	"
0.20	0.80	0.110	0.91	3.07	"
0.30	0.70	0.055	1.31	2.77	"
0.50	0.50	-0.055	3.09	1.42	"
0.70	0.30	-0.065	3.09	1.42	"
0.80	0.20	-0.050	3.68	0.98	"
0.90	0.10	-0.030	4.31	0.51	"

TABLE 65.

Amounts of the individual components at the interface for the cyclohexane system.

Solvent and solute molecules oriented parallel to surface.

M.F. of acid x_2	M.F. of cyc. x_1	Surface excess	Γ_1^s acid	Γ_1^s cyclohexane	
0.05	0.95	-0.01	0.16	3.35	μ moles/sq.m.
0.10	0.90	-0.02	0.33	3.23	"
0.20	0.80	-0.04	0.69	2.98	"
0.30	0.70	-0.06	1.07	2.72	"
0.50	0.50	-0.10	1.93	2.13	"
0.70	0.30	-0.10	2.96	1.42	"
0.80	0.20	-0.09	3.56	1.00	"
0.90	0.10	-0.06	4.23	0.54	"

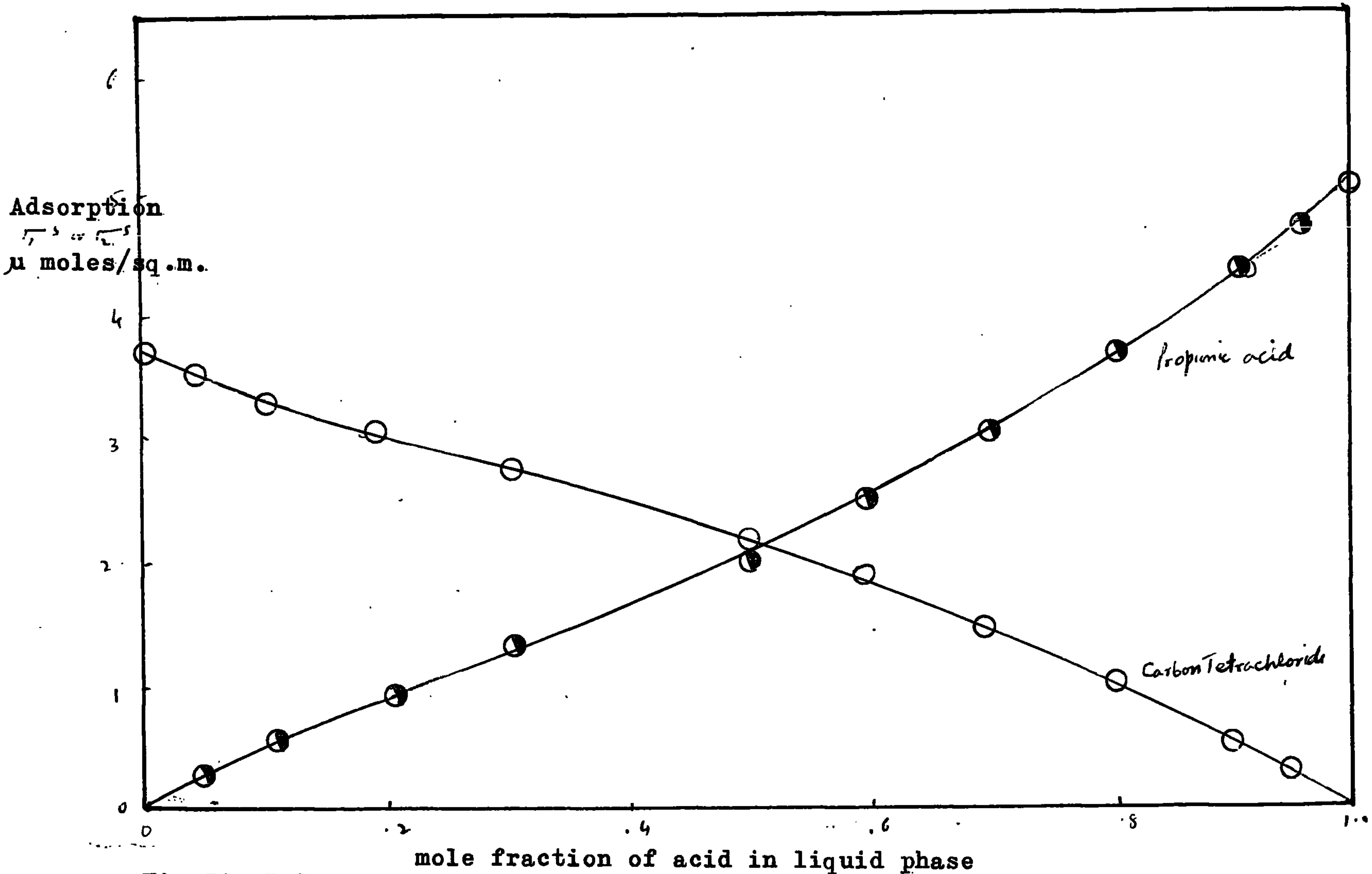
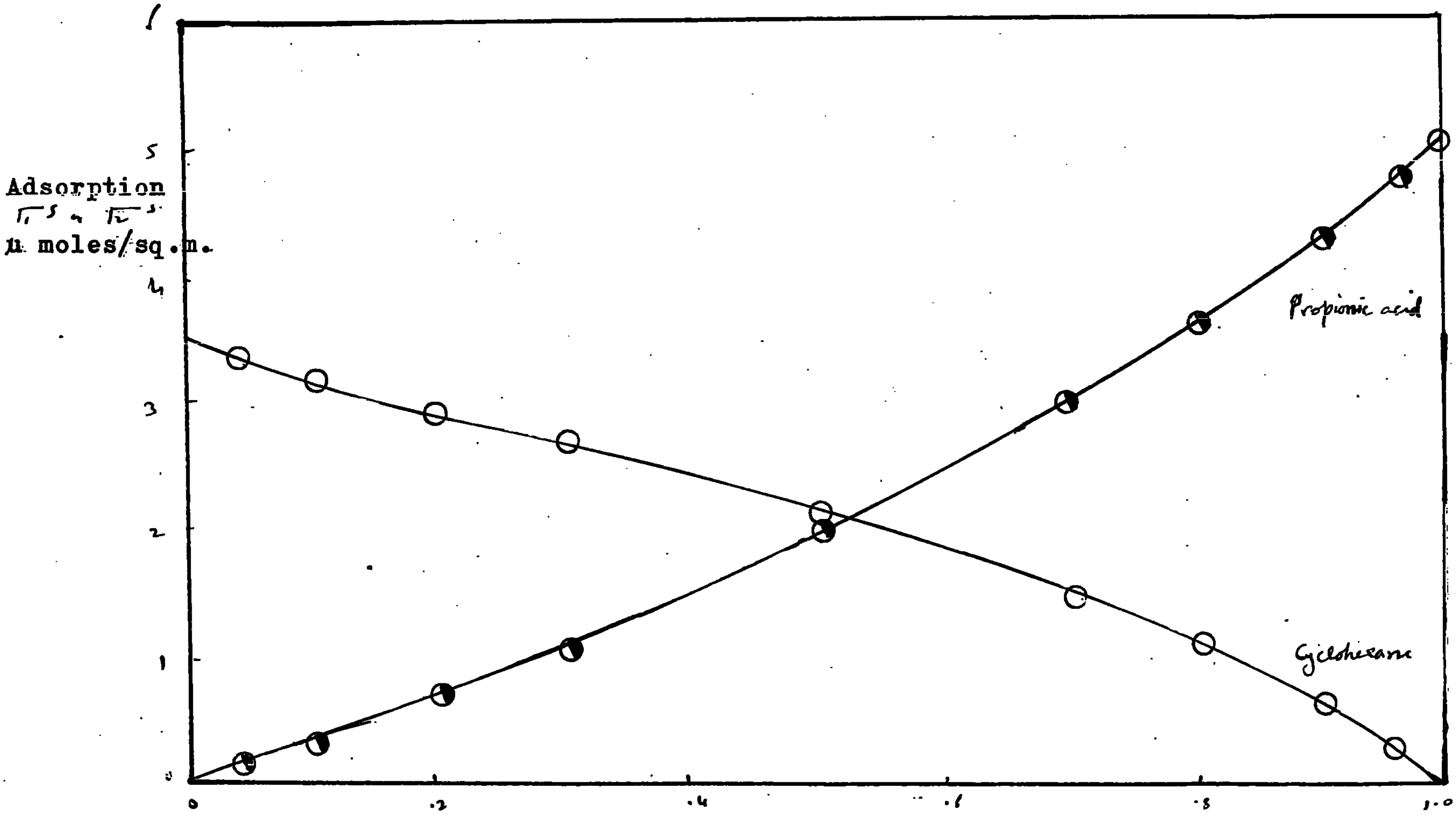


Fig.50- Individual isotherms for adsorption of propionic acid and carbon tetrachloride with the major axes of both molecules parallel to surface.



mole fraction of acid in liquid phase

Fig.51- Individual isotherms for adsorption of propionic acid and cyclohexane with the major axes of both molecules parallel to surface.

TABLE 66.

Amounts of the individual components at the interface for the propionic acid + ethyl alcohol system.

Solvent and solute molecules oriented perpendicularly.

M.F. of acid x_2	M.F. of ethanol	surface excess	Γ_2^s acid	Γ_1^s ethanol	
0.05	0.95	-0.200	0.18	7,38	μ moles/sq.m.
0.10	0.90	-0.360	0.39	7.20	"
0.20	0.80	-0.480	1.04	6.57	"
0.30	0.70	-0.510	1.78	5.87	"
0.50	0.50	-0.450	3.44	4.34	"
0.70	0.30	-0.340	5.11	2.60	"
0.90	0.10	-0.140	7.00	0.93	"

TABLE 67.

Amounts of the individual components at the interface for the propionic acid + water system.
Solvent and solute molecules oriented perpendicularly.

M.F. of acid x_2	M.F. of water	surface excess	Γ_2^s acid	Γ_1^s water	
0.05	0.95	4.25	4.78	6.80	μ moles/sq.m.
0.10	0.90	4.00	5.06	6.29	"
0.20	0.80	3.60	5.60	5.17	"
0.30	0.70	3.20	6.18	4.00	"
0.50	0.50	2.30	6.94	2.42	"
0.70	0.30	1.50	7.54	1.27	" "
0.80	0.20	1.00	7.72	0.80	"
0.90	0.10	0.55	7.98	0.34	"

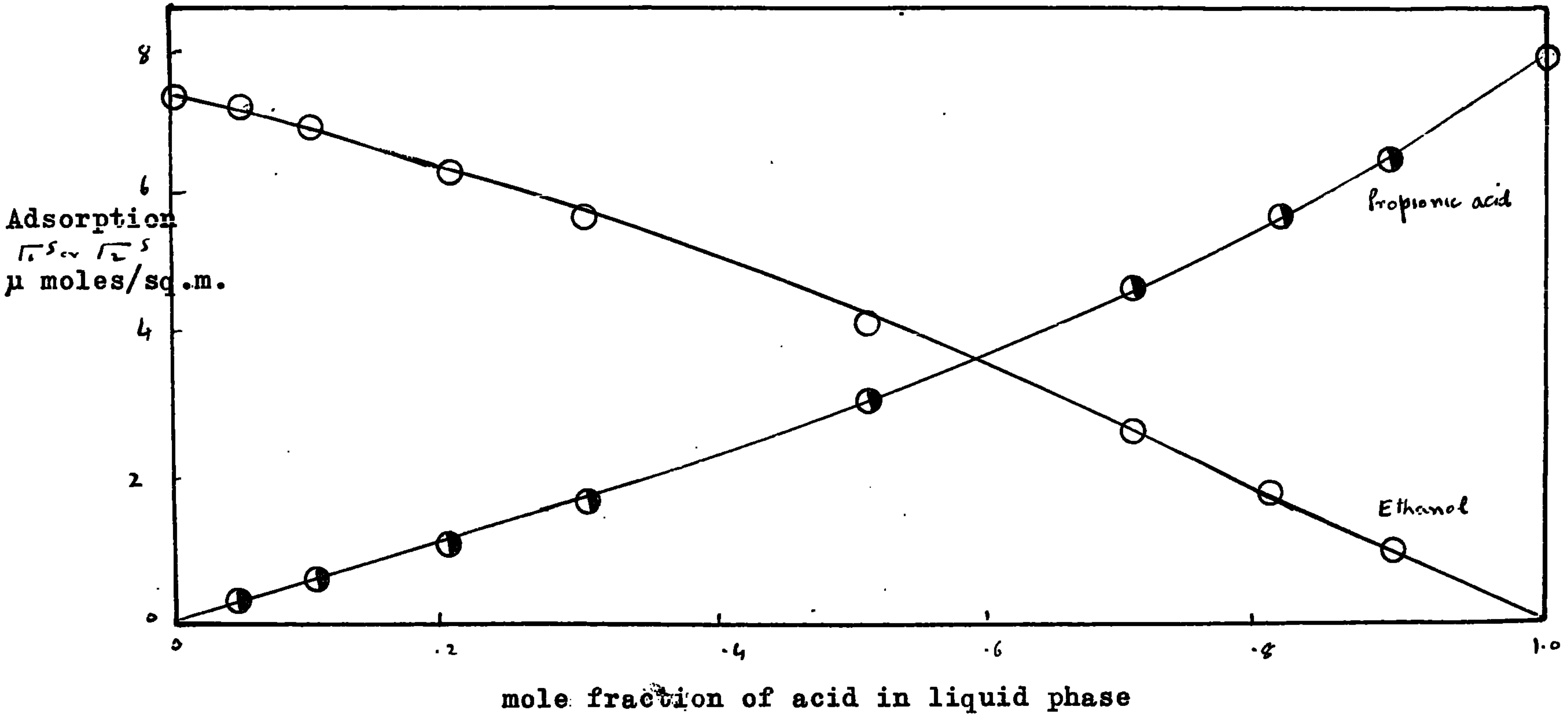


Fig.52– Individual isotherms for adsorption of propionic acid and ethanol with the major axes of both molecules perpendicular to the surface.

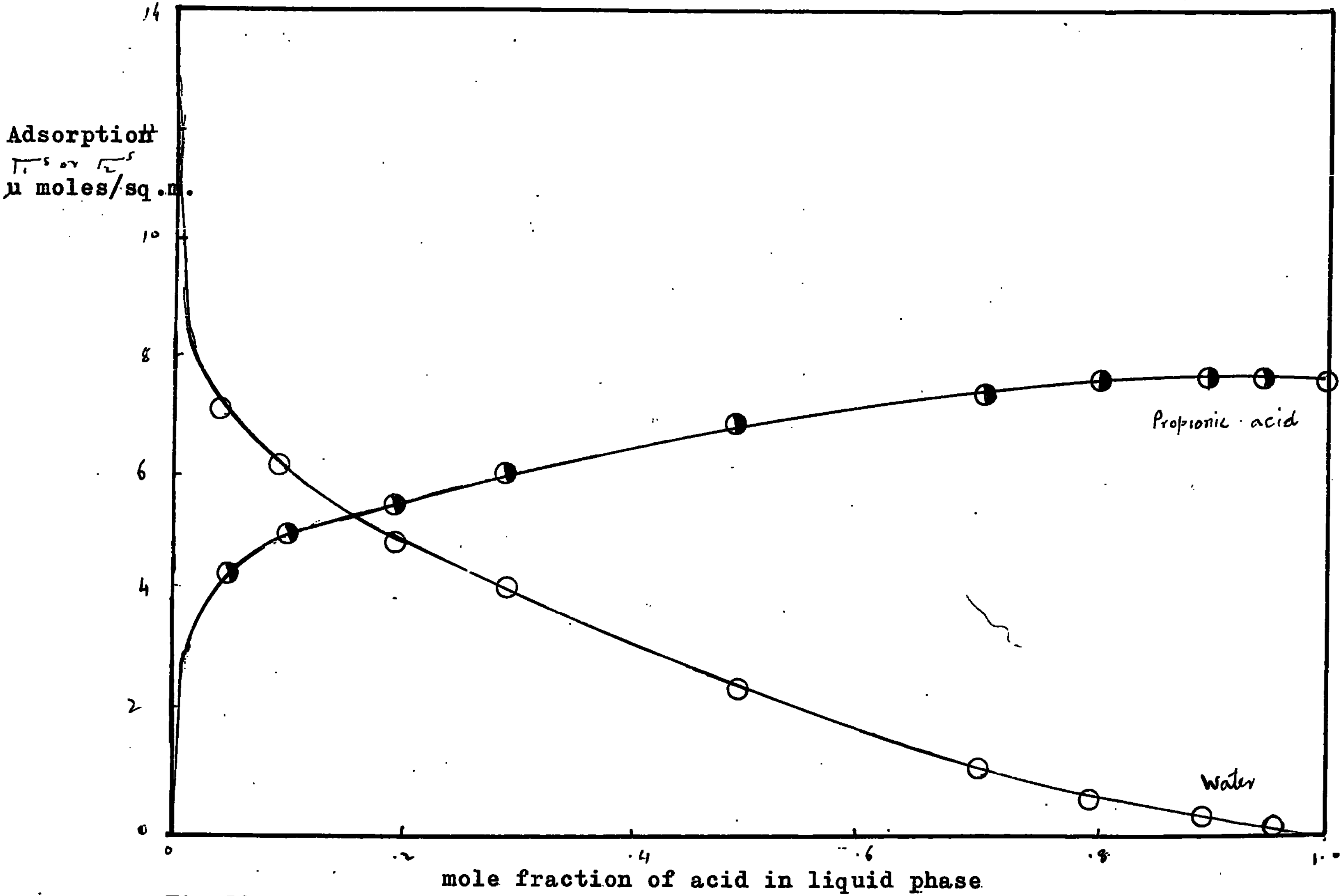


Fig.53- Individual isotherms for adsorption of propionic acid and water with the major axes of both molecules perpendicular to the surface.

TABLE 68.

Amounts of the individual components at the interface for the butyric acid + benzene system.

Solvent and solute molecules oriented parallel to surface.

M.F. of acid x_2	M.F. of benz. x_1	Surface excess	Γ_2^s acid	Γ_1^s benzene	
0.05	0.95	0.15	0.34	3.55	μ moles/sq.m.
0.10	0.90	0.21	0.60	3.33	"
0.20	0.80	0.25	1.05	2.93	"
0.30	0.70	0.25	1.45	2.56	"
0.45	0.55	0.24	2.09	2.11	"
0.60	0.40	0.19	2.69	1.48	"
0.70	0.30	0.16	3.11	1.08	"
0.80	0.20	0.11	3.52	0.744	"
0.90	0.10	0.05	3.93	0.38	"

TABLE 69.

Amounts of the individual components at the interface for the carbon tetrachloride system.

Solvent and solute molecules oriented parallel to surface.

M.F. of acid x_2	M.F. of CCl_4 x_1	surface excess	Γ_2^s acid	Γ_1^s CCl_4	
0.05	0.95	+0.150	0.33	3.41	μ moles/sq.m.
0.10	0.90	+0.140	0.52	3.25	"
0.20	0.80	+0.100	0.93	3.00	"
0.30	0.70	+0.050	1.36	2.68	"
0.45	0.55	-0.045	1.73	2.22	"
0.60	0.40	-0.520	2.38	1.68	"
0.70	0.30	-0.040	2.85	1.28	"
0.80	0.20	-0.030	3.33	0.87	"
0.90	0.10	-0.020	3.92	0.46	"

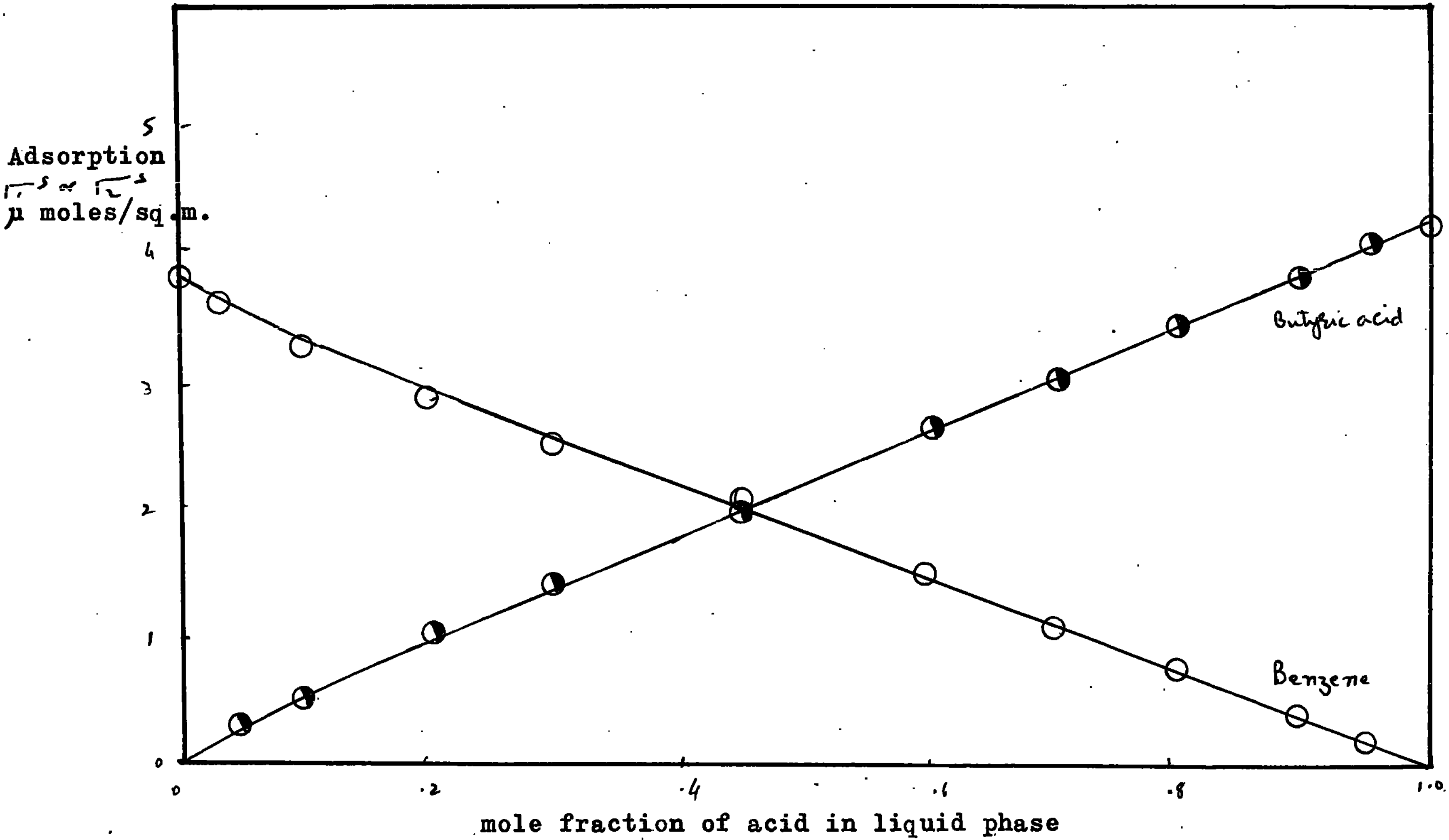


Fig.54- Individual isotherms for adsorption of butyric acid and benzene with the major axes of both molecules parallel to surface.

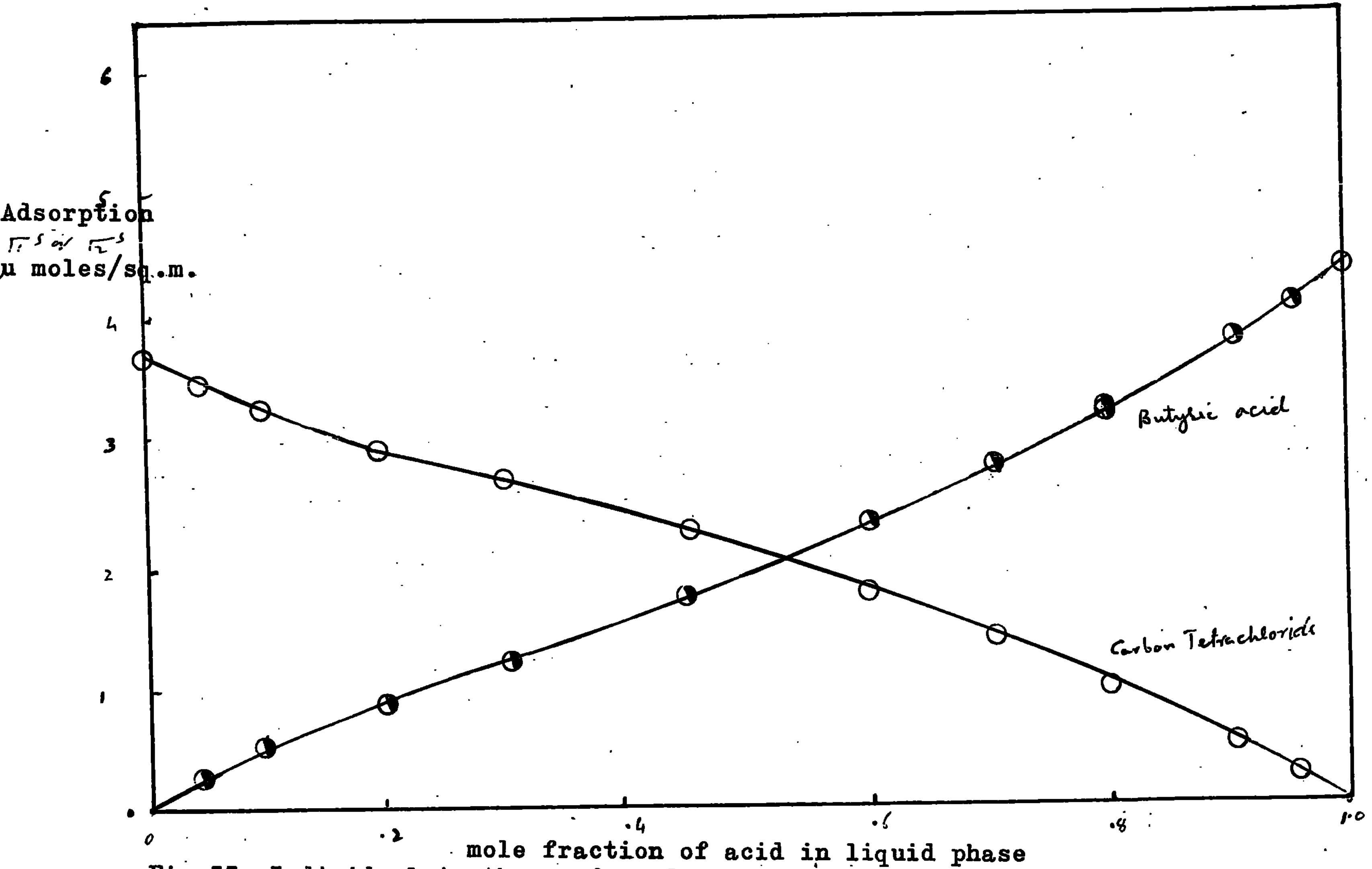


Fig.55- Individual isotherms for adsorption of butyric acid and carbon tetrachloride with the major axes of both molecules parallel to surface.

TABLE 70.

Amounts of the individual components at the interface for the butyric acid + cyclohexane system.

Solvent and solute molecules oriented parallel to surface.

M.F. of acid x_2	M.F. of cyc. x_1	surface excess	Γ_2^s acid	Γ_1^s cyclohexane	
0.05	0.95	-0.030	0.156	3.33	μ moles/sq.m.
0.10	0.90	-0.045	0.300	3.21	"
0.20	0.80	-0.060	0.660	2.94	"
0.30	0.70	-0.080	1.021	2.65	"
0.45	0.55	-0.102	1.600	2.19	"
0.60	0.40	-0.111	2.245	1.68	"
0.70	0.30	-0.115	2.700	1.32	"
0.80	0.20	-0.105	3.200	0.93	"
0.90	0.10	-0.065	3.85	0.500	"

TABLE 71.

Amounts of the individual components at the interface for the butyric acid + water system.

Solvent and solute molecules oriented perpendicularly.

M.F. of acid x_2	M.F. of water x_1	surface excess	Γ_2^s acid	Γ_1^s water	
0.05	0.95	4.50	5.06	6.22	μ moles/sq.m.
0.10	0.90	4.05	5.17	6.01	"
0.20	0.80	3.30	5.47	5.39	"
0.30	0.70	2.50	5.69	4.94	"
0.45	0.55	1.50	6.09	4.11	"
0.60	0.40	0.90	6.66	2.94	"
0.70	0.30	0.50	6.99	2.28	"
0.90	0.10	0.10	7.75	0.75	"

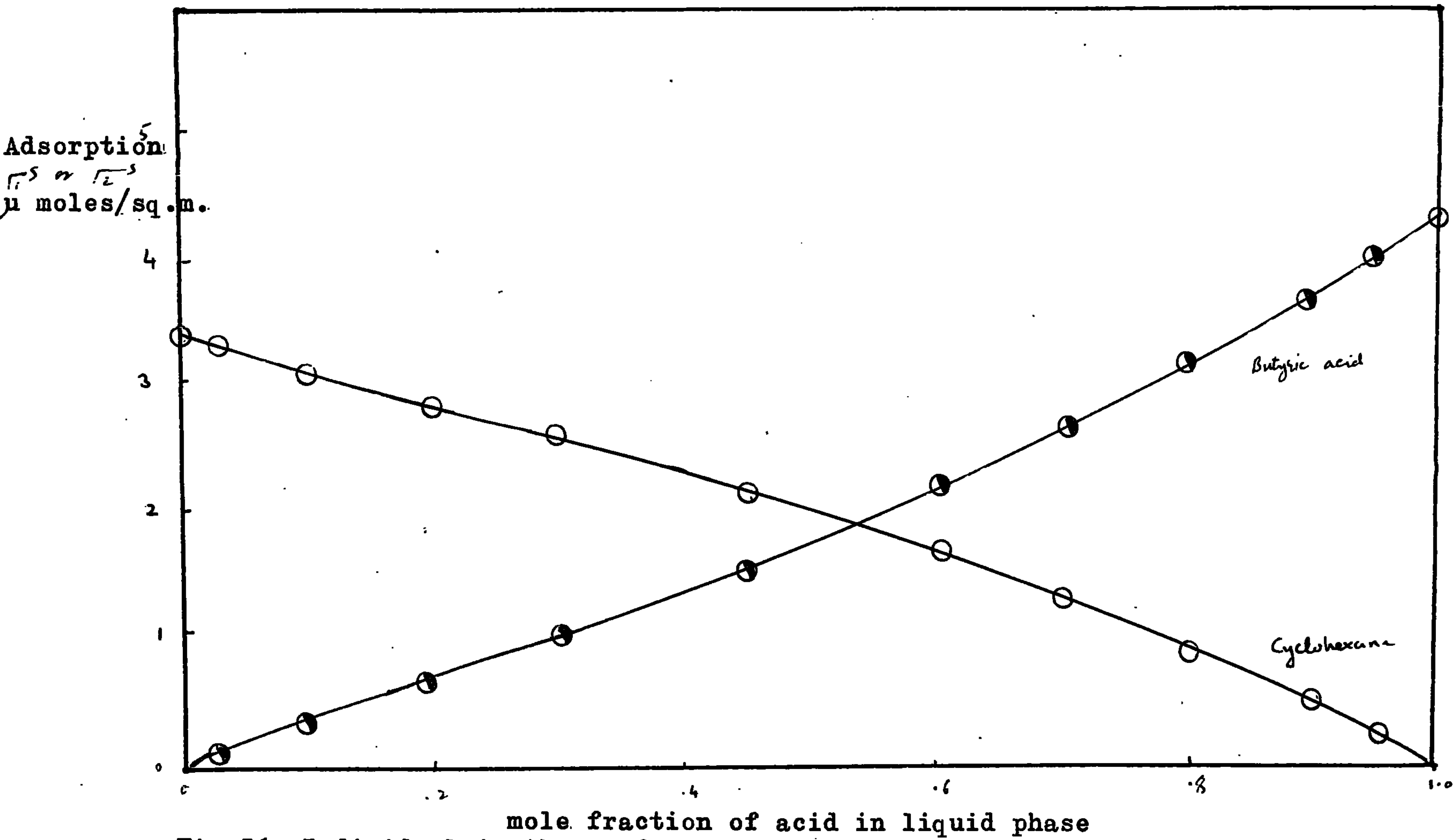


Fig.56- Individual isotherms for adsorption of butyric acid and cyclohexane with the major axes of both molecules parallel to the surface.

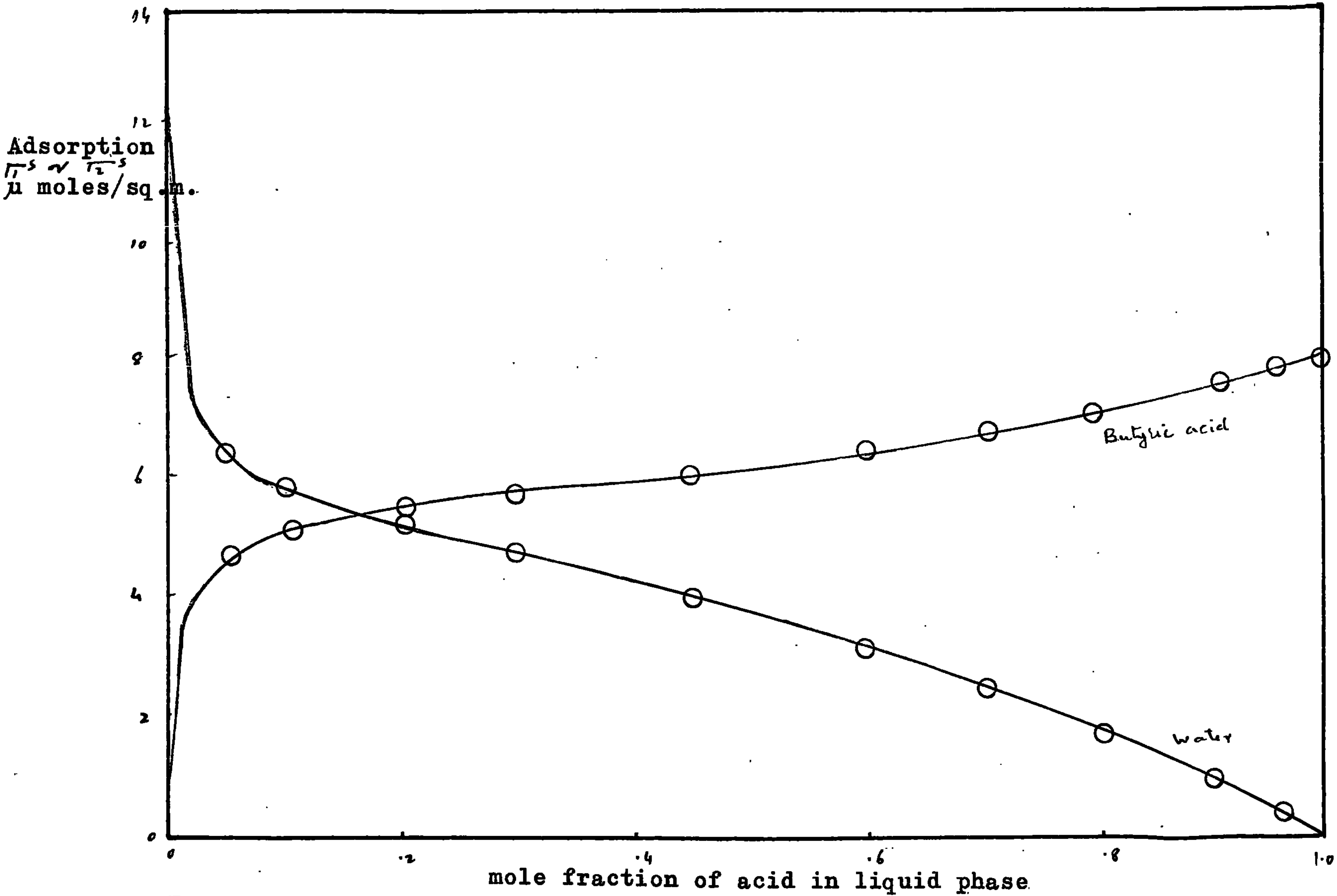


Fig.57– Individual isotherms for adsorption of butyric acid and water at 30 C with the major axes of both molecules perpendicular to the surface.

TABLE 72

The fractions of the surface covered by acetic acid in five systems at different concentrations of acid in the liquid phase.

M.F. of acid x_2	$\frac{\Gamma_2}{(\Gamma_2)_m}$ water	$\frac{\Gamma_2}{(\Gamma_2)_m}$ benzene	$\frac{\Gamma_2}{(\Gamma_2)_m}$ CCl_4	$\Gamma_2/(\Gamma_2)_m$ cyclohexane	$\Gamma_2/(\Gamma_2)_m$ ethanol.
0.10	0.706	0.100	0.086	0.080	0.078
0.20	0.781	0.171	0.156	0.130	0.125
0.30	0.836	0.215	0.200	0.201	0.199
0.50	0.900	0.410	0.360	0.349	0.330
0.70	0.960	0.573	0.556	0.534	0.522
0.80	0.982	0.700	0.685	0.664	0.650
0.95	0.994	0.920	0.913	0.888	0.880

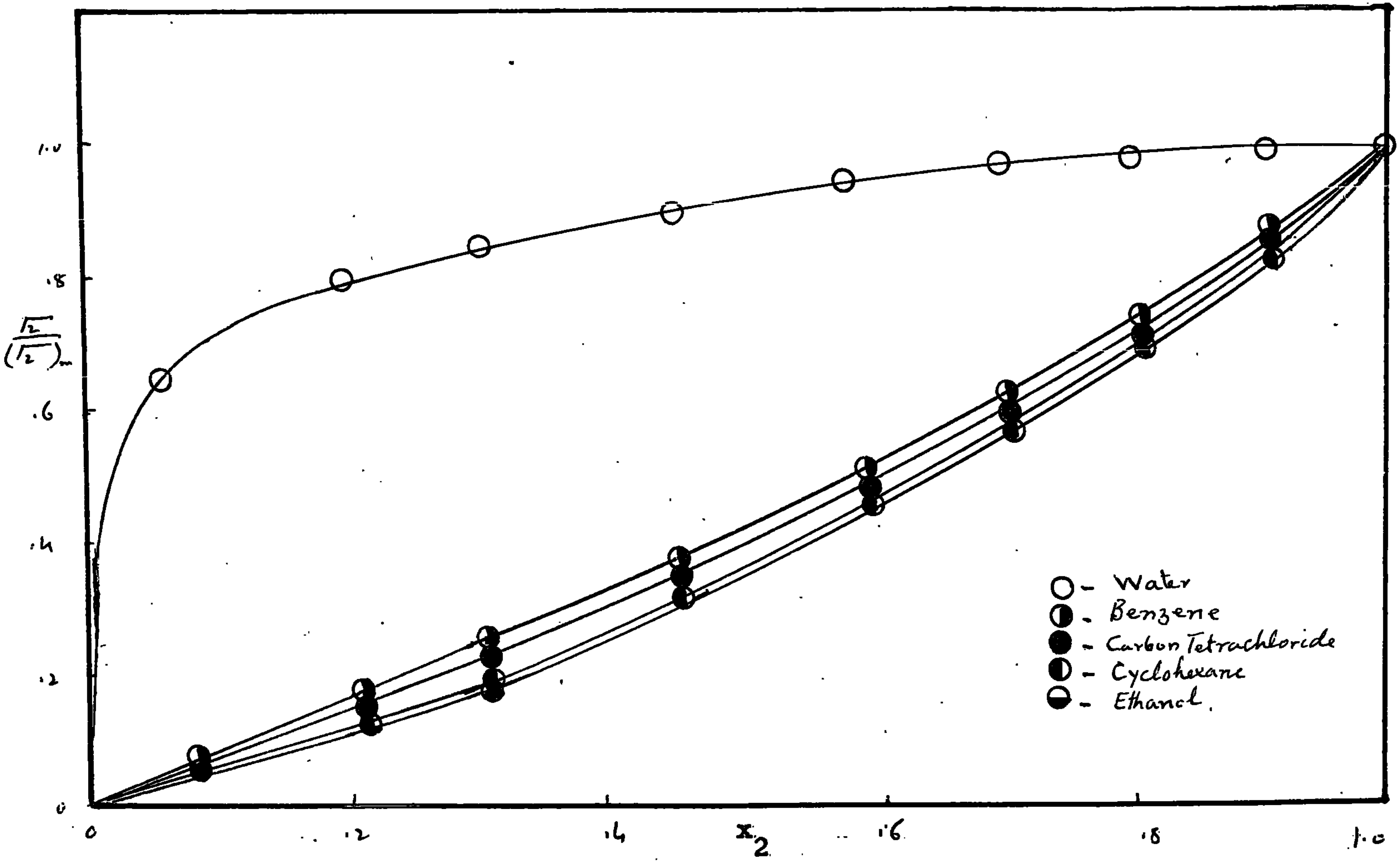


Fig.58- Fractions of the surface covered by acetic acid in five systems.

TABLE 73.

The fractions of the surface covered by propionic acid in five systems at different concentrations of acid in the liquid phase.

M.F. of acid x_2	$\Gamma_2/\Gamma_2)_m$ water	$\Gamma_2/\Gamma_2)_m$ benzene	$\Gamma_2/\Gamma_2)_m$ CCl_4	$\Gamma_2/\Gamma_2)_m$ cyclohexane	$\Gamma_2/\Gamma_2)_m$ ethanol
0.10	0.622	0.107	0.100	0.070	0.500
0.20	0.692	0.204	0.174	0.137	0.120
0.30	0.758	0.293	0.250	0.213	0.200
0.50	0.854	0.480	0.411	0.384	0.370
0.70	0.922	0.675	0.616	0.589	0.510
0.80	0.951	0.775	0.733	0.710	0.650
0.90	0.980	0.882	0.860	0.842	0.781
0.95	0.987	0.932	0.920	0.920	0.872

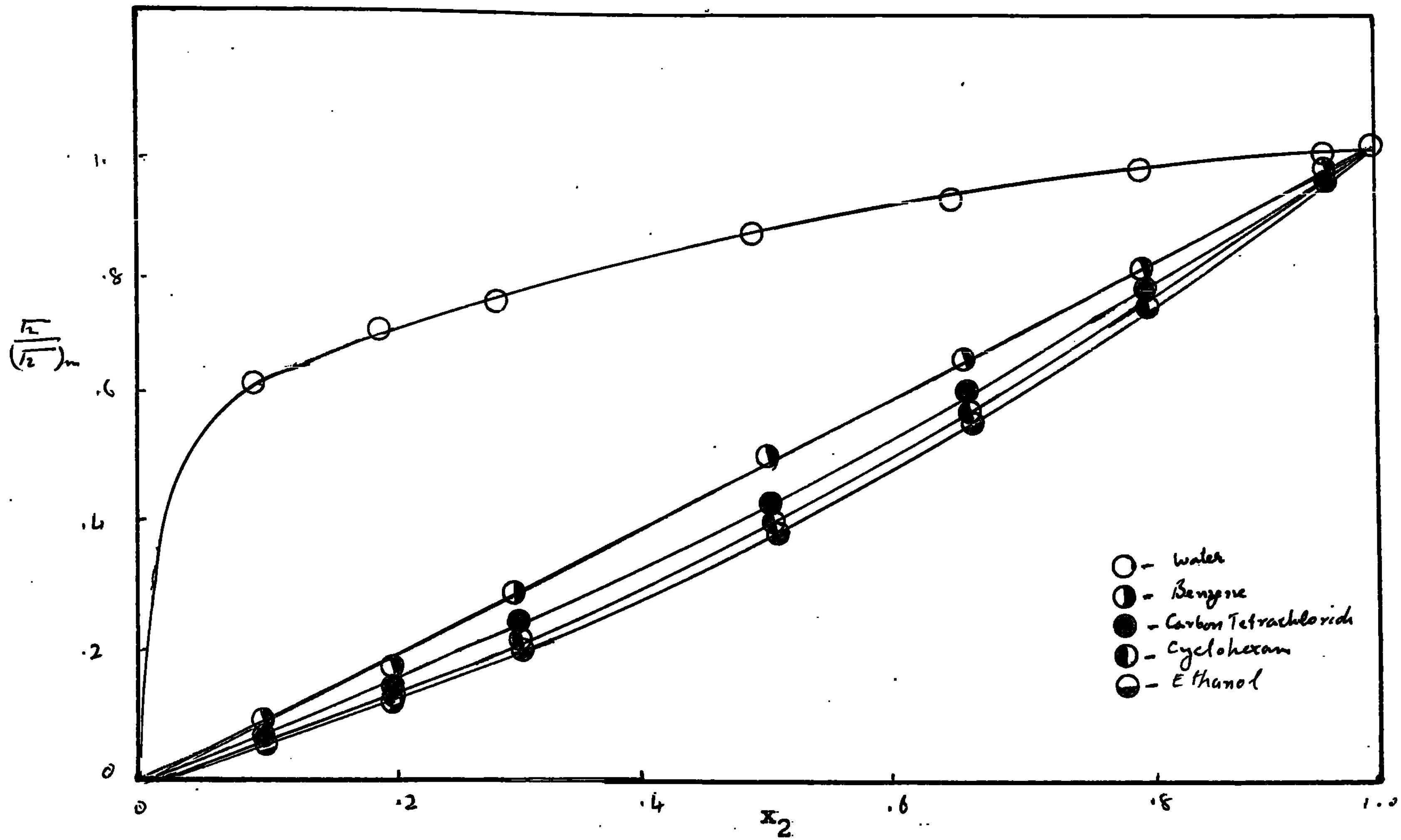


Fig.59- Fractions of the surface covered by propionic acid in five systems.

TABLE 74.

The fractions of the surface covered by butyric acid in four systems at different concentrations of acid in the liquid phase.

M.F. of acid x_2	$\Gamma_2/\Gamma_2)_m$ water	$\Gamma_2/\Gamma_2)_m$ benzene	$\Gamma_2/\Gamma_2)_m$ CCl_4	$\Gamma_2/\Gamma_2)_m$ cyclohexane
0.10	0.637	0.138	0.118	0.070
0.20	0.675	0.239	0.193	0.149
0.30	0.702	0.333	0.272	0.233
0.45	0.752	0.477	0.396	0.366
0.60	0.823	0.616	0.544	0.520
0.70	0.862	0.713	0.652	0.618
0.80	0.905	0.810	0.762	0.732
0.90	0.956	0.899	0.897	0.861
0.95	0.979	0.950	0.933	0.929

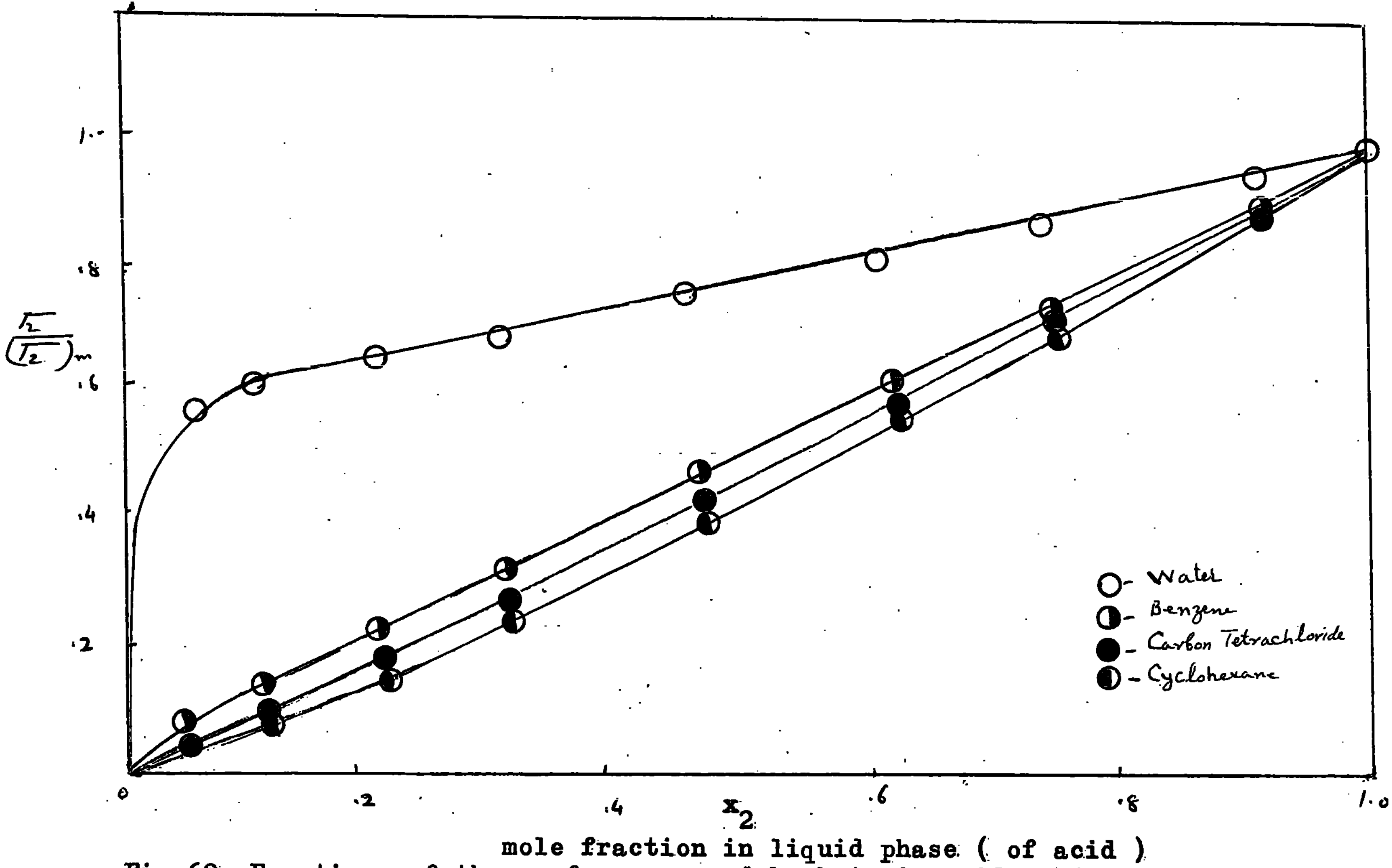
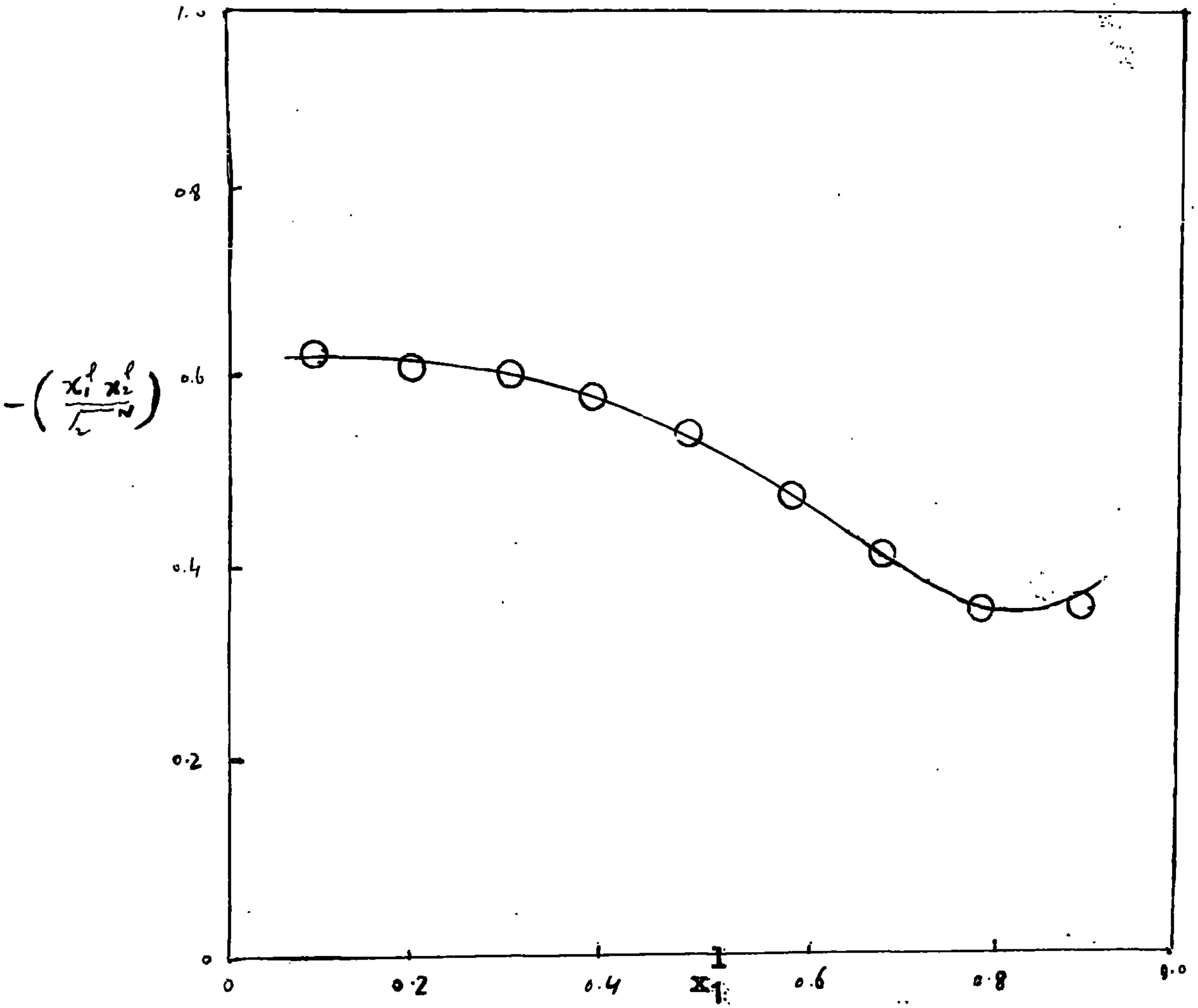


Fig.60– Fractions of the surface covered by butyric acid in four systems.

TABLE 75.

Composite Isotherms and Adsorption Equilibrum
Propionic acid + Ethanol system.

M.F. of eth. x_1^l	M.F. of acid x_2^l	$x_1^l\ x_2^l$	surface excess	$\frac{x_1^l x_2^l}{\Gamma_2^N}$
0.10	0.90	0.09	-0.14	-0.64
0.20	0.80	0.16	-0.26	-0.62
0.30	0.70	0.21	-0.34	-0.61
0.40	0.60	0.24	-0.41	-0.59
0.50	0.50	0.25	-0.45	-0.55
0.60	0.40	0.24	-0.50	-0.48
0.70	0.30	0.21	-0.50	-0.42
0.80	0.20	0.16	-0.45	-0.35
0.90	0.10	0.09	-0.25	-0.36



mole fraction of alcohol in liquid phase

Fig.61- Adsorption at 30°C from solutions of propionic acid + ethyl alcohol.

TABLE 76.

Composite Isotherm and Adsorption Equilibrium Butyric acid + Benzene system.

M.F. of benz. x_1^l	M.F. of acid x_2^l	$x_1^l\ x_2^l$	surface Excess	$\frac{x_1^l\ x_2^l}{\Gamma_2^N}$
0.10	0.90,	0.09	0.06	1.50
0.20	0.80	0.16	0.12	1.33
0.30	0.70	0.21	0.16	1.30
0.40	0.60	0.24	0.20	1.20
0.50	0.50	0.25	0.22	1.13
0.60	0.40	0.24	0.25	0.96
0.70	0.30	0.21	0.25	0.84
0.80	0.20	0.16	0.25	0.64
0.90	0.10	0.09	0.20	0.45

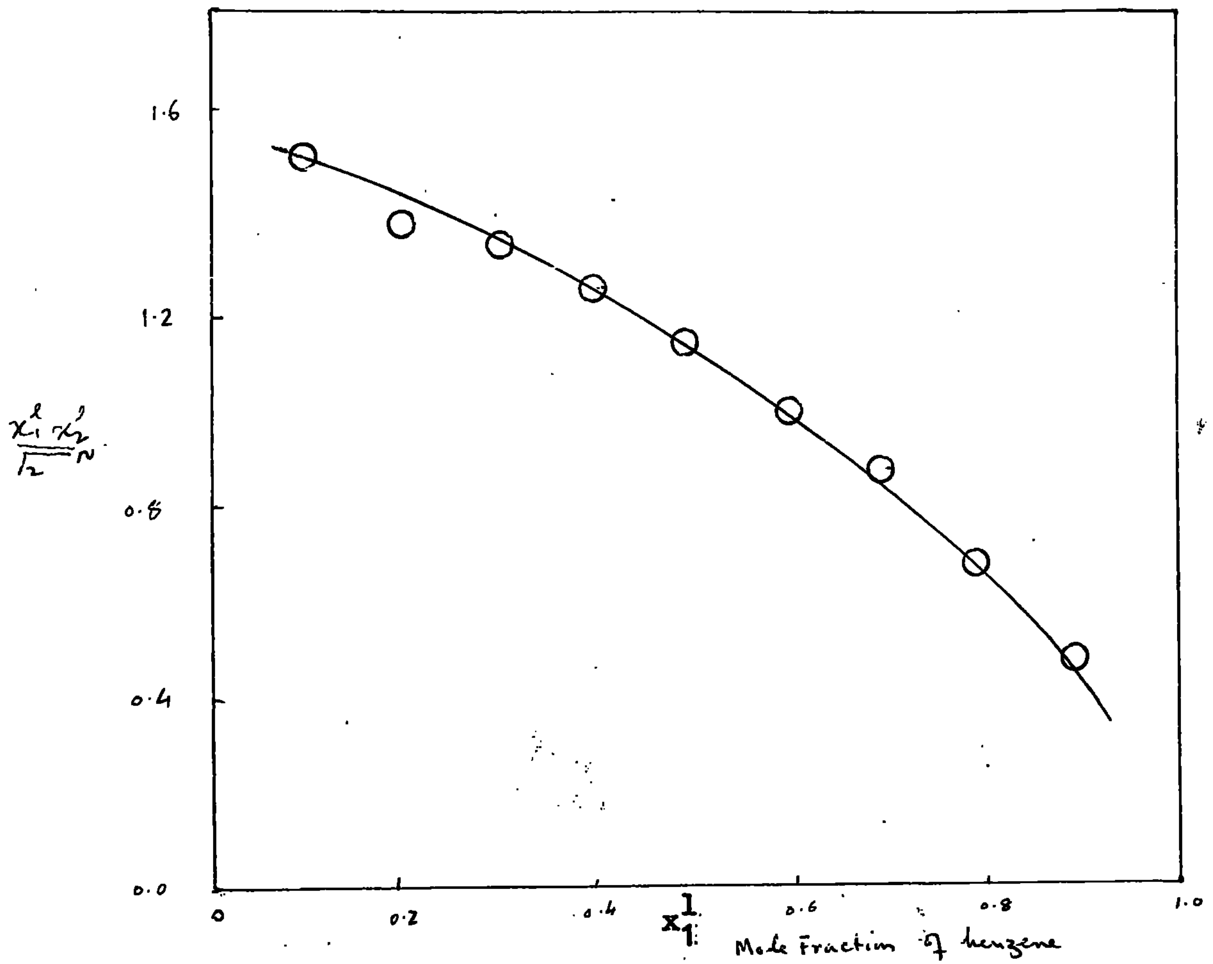


Fig.62- ~~Plot~~ Adsorption at 30°C from solutions of butyric acid + benzene.

CHAPTER 8

COMPOSITE ISOTHERMS.

(a) Acetic acid systems

1. **Benzene:** The composite isotherm, fig.17, for the system acetic acid + benzene is S-type and shows that the apparent adsorption of acid increases with increasing concentration of the acid in the liquid phase, reaches a maximum and then falls to zero. A negative adsorption of the acid is noted in the higher acid concentration region. So that at the lower concentrations we note preferential adsorption of the acid and at higher concentrations preferential adsorption of benzene. The highest value of Γ_2^n is about 0.2 μ moles/sq.m. and the lowest value is about -0.12 μ moles/sq.m. The shape of the composite isotherm is of the same type as that obtained by Belton[5] for acetic acid + benzene system.

2. **Carbon Tetrachloride.** The composite isotherm, fig.19, for the system acetic acid + carbon tetrachloride is also S-shaped. The apparent adsorption of the acid increases with the increasing acid concentration, reaches a maximum

value of about 0.125 μ moles/sq.m. at approximately 0.15 mole fraction of the acid in the liquid phase and then it begins to fall. Negative adsorption begins to occur between mole fraction 0.3 and 0.4 of acid, reaching minimum value of -0.2 μ moles/sq.m. between 0.5 and 0.6 mole fraction of the acid and then increases again and attains zero value at unit mole fraction. Thus, as for the acetic acid + benezene system there is preferential adsorption of acid at low mole fractions of acid in the liquid phase and preferential adsorption of carbon tetrachloride at the higher mole fractions. It may be noted that for this system the preferential adsorption of carbon tetrachloride at the higher concentrations is almost twice that of the acid at lower concentrations; again, preferential adsorption of acid occurs in only about one-third of the whole concentration range.

3. <u>Cyclohexane.</u> The composite isother, fig.21, for the system acetic acid + cyclohexane is again S-shaped. Preferential adsorption of acetic acid takes place at lower concentrations of the acid in the liquid phase, reaches a maximum value of about 0.08 μ moles per sq.m. at 0.5 mole

fraction and then starts falling to zero. With increasing acid concentration negative adsorption of the acid is noted, thus indicating preferential adsorption of cyclohexane. For this system preferential adsorption of acid occurs over about half the concentration range. The maximum value of apparent acid adsorption at low acid concentration is about half the value of preferential cyclohexane adsorption at high acid concentrations, and by comparing this isotherm with those for benzene and carbon tetrachloride it is noted that preferential adsorption of acid is low in this system.

4. Ethyl alcohol. The composite isotherm, fig.23, for acetic acid + alcohol system is a regular U-shaped curve, showing a negative adsorption for the acid over the whole range of acid concentration in the liquid phase. This indicates preferential adsorption of ethyl alcohol throughout, a situation not encountered with any of the other acetic acid systems, and arising out of the unique ability of ethyl alcohol + acetic acid mixtures throughout the whole concentration range. The maximum preferential adsorption of alcohol as seen from the composite isotherm is high and about

0.48 µ moles/sq.m., occurring between 0.3 and0.5 mole fraction of acid in the liquid phase.

5. Water. The composite isotherm, fig.25, of the system acetic acid + water is an inverted U-shaped type. The preferential adsorption of the acid is very high even at very low concentrations of the acid in the liquid phase. This preferential adsorption of the acid decreases almost linearly with increasing acid concentration in the liquid phase but the isotherm does not show a negative adsorption of the acid over any concentration region. If the maximum in preferential adsorption of the acid for this system is compared with those for the other systems, it will be noted that acetic acid shows its highest adsorption, approximately 4.0 µ moles/sq.m. in this system. One may expect the acid and water to have strong intermoleculer interactions, and it seems likely that the nature of the interface for the system is markedly different from that of acetic acid with the solvents benzene, carbon tetrachloride and cyclohexane. This point will be further discussed later.

(b) Propionic acid systems.

1. Benzene. The composite isotherm, fig.27, for the propionic acid + benzene system shows preferential adsorption of propionic acid throughout the whole concentration range. This may be contrasted with the corresponding acetic acid system for which there is preferential adsorption of both acetic acid and benzene at different regions along the concentration axis. The apparent adsorption of propionic acid is higher at the lower concentrations than at the higher concentrations of acid in the liquid phase and higher than for acetic acid at all concentrations. The maximum preferential adsorption of the acid as indicated by this isotherm is approximately 0.22 μ moles/sq.m. (cf. the maximum of 0.20 μ moles/sq.m. for the corresponding acetic system).

2. Carbon tetrachloride. The composite isotherm, fig. 29, of the propionic acid + carbon tetrachloride system is S-shaped. The isotherm indicates preferential adsorption of acid at the lower concentrations of acid in the liquid phase, but preferential adsorption of carbon tetrachloride at the higher concentrations. The maximum of preferential adsorption of the acid is about 0.13 μ moles/sq.m. and the minimum about -0.075 μ moles/sq.m. and the isotherm is

similar to that for the acetic acid + carbon tetrachloride system, but for the propionic acid + carbon tetrachloride system preferential adsorption of acid is slightly greater than that for the acetic acid + carbon tetrachloride system. It is noted that the preferential adsorption of carbon tetrachloride is much lower in this system as compared with acetic acid system, thus indicating a greater amount of acid in the adsorbed phase for the propionic acid system.

3. Cyclohexane. The composite isotherm, fig.31, for the propionic acid + cyclohexane system is U-shaped, and shows a negative adsorption of the acid over the whole range of acid concentration in the liquid phase. This indicates preferential adsorption of cyclohexane at the interface. The preferential adsorption of cyclohexane increases with the increasing acid concentration in the liquid phase, reaches a maximum value at very high concentration and then falls to zero. The maximum in preferential adsorption of cyclohexane, approximately 0.12 μ moles/sq.m. occurs between 0.6 and 0.8 mole fraction of the acid in the liquid phase. It should be noted that the

correspondibg acetic acid isotherm is not U-shaped but S-shaped, andthat preferential adsorption for acetic acid occurs over about half the concentration range.

4. Ethyl alcohol. The composite isotherm, fig.33, for propionic acid + ethyl alcohol is U-shaped, and shows negative adsorption of acid over the whole range of acid concentration in the liquid phase. This indicates preferential adsorption of ethyl alcohol throughout, and is similar to the corresponding acetic acid system. The preferential adsorption of alcohol increases with the increasing acid concentrations in the liquid phase, reaches a maximum and then falls to zero. The maximum value of alcohol adsorption, approximately 0.5 µ moles per sq.m. occurs between the mole fractions 0.25 and 0.45 of the acid in the liquid phase. It may be noted that the value of the maximum preferential adsorption of ethyl alcohol is about the same in this system as in acetic acid + alcohol system.

5. Water. The composite isotherm, fig. 35, of the propionic acid + water system is an inverted U-shaped

isotherm, similar to that of the corresponding acetic acid system. The adsorption of acid is very high at quite low concentrations of the acid in the liquid phase, but this preferential adsorption of the acid decreases with increasing acid concentration in the liquid phase. The isotherm does not show a negative adsorption of acid at any concentration. The value of maximum preferential adsorption of acid, approximately 4.3 μ moles/sq.m. is higher than that for the acetic acid + water system (4.0 μ moles/sq.m.)

(c) n-Butyric acid systems.

1. Benzene. Fig.37 shows the composite isotherm for the butyric acid + benzene system. The apparent adsorption of the acid increases with increasing acid concentration in the liquid phase, reaches a maximum, then begins to fall to zero. In this system only positive adsorption of the acid is noted, indicating preferential adsorption of acid at all concentrations, as is the case for the corresponding Propionic acid system. The maximum value of preferential adsorption of acid indicated by the isotherm (about 0.26 μ moles/sq.m.) is higher than the corresponding values of adsorption of the other two acids in this solvent (0.2 μ moles/sq.m. for acetic acid and 0.22 μ moles/sq.m. for propionic acid).

2. Carbon tetrachloride. The composite isotherm, fig.39, for the system butyric acid + carbon tetrachloride is S-shaped, showing both positive and negative apparent adsorption of the acid. The adsorption of the acid increases with the increasing acid content, reaches a maximum and then begins to fall, after which negative adsorption of the acid is noted. So at the lower concentrations of the acid in the liquid phase it is the acid which is preferentially adsorbed, but at higher concentrations carbon tetrachloride is preferentially adsorbed. This is similar to the corresponding propionic acid and acetic acid systems. The maximum value of the acid adsorption is about 0.15 μ moles/sq.m. and the minimum value is about-0.07 μ moles/sq.m. It is noted that the apparent adsorption of acid, after attaining a maximum value at low acid concentrations in the liquid phase falls almost linearly between a concentration range of 0.1 and 0.4 mole fraction of acid in the liquid phase. Schay and Nagy considered that this is most probably due to Γ_1^s and Γ_2^s remaining constant over that section of the isotherm,[37] i.e. that for the range of concentration over which the

isotherm is linear and of negative gradient, the composition of the adsorbed phase remains constant.

3. Cyclohexane. Fig.41 shows the composite isotherm for the system butyric acid + cyclohexane. It is a U-shaped isotherm, and shows negative acid adsorption over the whole range of acid concentration in the liquid phase. This indicates preferential adsorption of cyclohexane over the whole concentration range. The preferential adsorption of cyclohexane increases with increasing acid concentration in the bulk phase, reaches a rather broad maximum at a high concentration and then falls to zero. The maximum values of preferential cyclohexane adsorption occurs between 0.5 and 0.8 mole fractions of the acid in the liquid phase. The isotherm is similar to that for the corresponding propionic acid system.

4. Water. The composite isotherm, fig.43, for the system butyric acid + water is an inverted U-shaped curve, similar to the isotherms for the corresponding propionic acid and acetic acid systems. The preferential adsorption of the acid is very high at low concentration of acid in the liquid phase, attains a maximum, and then decreases with increasing acid concentration in the bulk. The isotherm does not show

a negative adsorption of acid at any concentration, this indicating preferential adsorption of the acid throughout. The value of maximum preferential adsorption, nearly 4.5 μ moles/sq.m. is higher than those for the corresponding propionic and acetic acid values. (4.0 μ moles/sq.m. for acetic and 4.3 μ moles/sq.m. for propionic acid).

CHAPTER 9.

Molecular Areas of adsorbed Species.

A knowledge or molecular areas of the adsorbed species is essential for obtaining the individual isotherms from the composite (surface excess) isotherms. In this chapter, possible values of the molecular areas are discussed, keeping in mind the possibility of both parallel and perpendicular orientations, where applicable. The molecular areas of some of the molecules, for a particular orientations, have been taken from the literature, whereas others have been calculated from bond angles and bond lengths.

In so far as choosing an appropriate molecular area for a particular molecule in the calculation of individual isotherms is concerned, one has to consider various factors such as the possible interactions between the components of the solution at the interface and also the overall nature of the composite isotherm concerned. The set of individual isotherms obtained by choosing a given molecular area for a component often reveals if such a choice is a reasonable one.

The area of the water molecule, has been taken as 10 sq.A which is the generally accepted value.[7,23] The area per molecule of propionic or butyric acid with major axis perpendicular to the surface, has been taken as 20.5 sq. A.[12]

Area of carbon tetrachloride molecule[38] (Fig.63)

Van der Waals' radius for Cl = 1.80A.

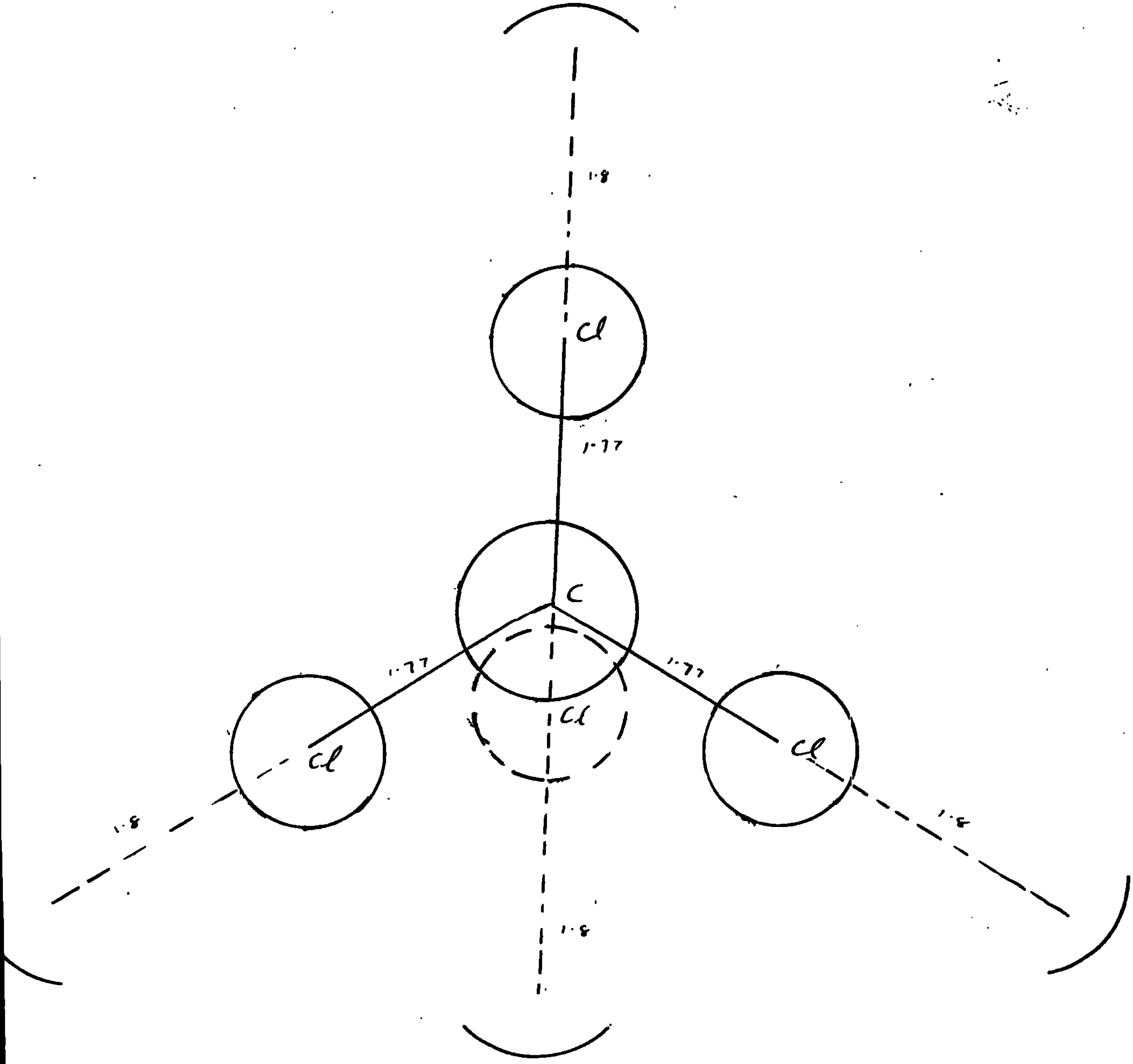
Distance C--Cl = 1.77A.

The molecule is almost spherical, hence its area can be calculated as

$$
\begin{aligned}
\text{Area} &= \pi\,(1.77 + 1.80)^2 \\
&= \pi\,(3.57)^2 \\
&= 40.04 \text{ sq.A.}
\end{aligned}
$$

The isotherms in this work have been obtained at 30°C, and at this temperature work with carbon tetrachloride at various interfaces has shown that a value of 45.0 sq.A per molecule is more reasonable for carbon tetrachloride. Hence the same value has been used in this work.

CARBON TETRACHLORIDE MOLECULE Fig. 63



Area of benzene molecule. (Fig.64)

(i) Major axis parallel to the surface:

Van der Waals' radius for Hydrogen = 1.20A

Distance C----H = 1.084A

Distance C----C = 1.397A

$x = \cos 60\ (1.39) = 0.698$ A

$y = \cos 30\ (1.397) = 1.2098$ A

$z = \cos 30\ (1.084) = 0.938$ A

Length of the molecule = $(1.2+1.08+0.698+1.39+0.695+1.08+1.2)$

$= 7.36$ A

Width of the molecule = $(1.2+0.938+1.2098+1.2098+0.938+1.2)$

$= 6.697$ A

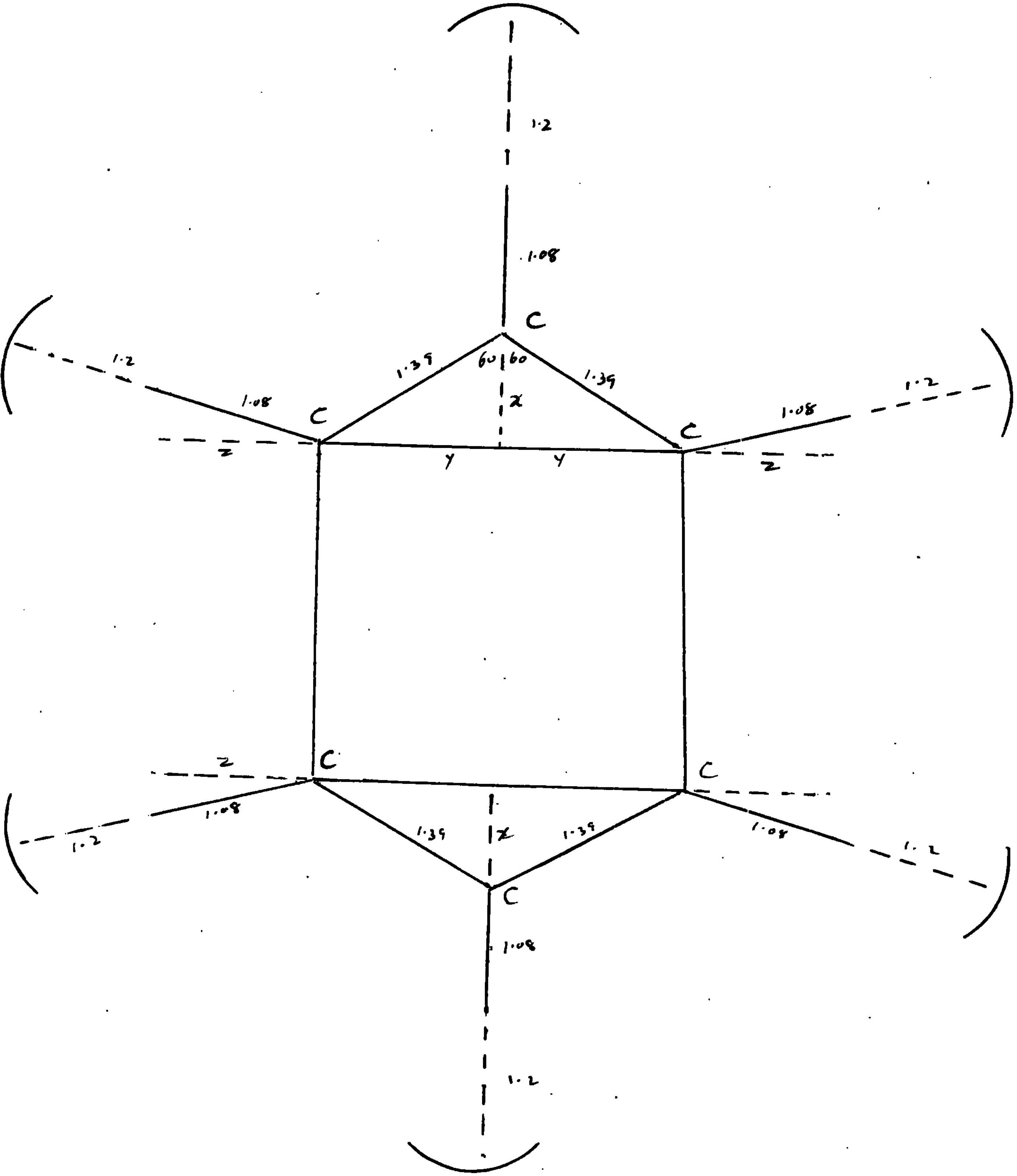
Area of the molecule = $6.697 \times 7.362 = 49.3$ sq.A.

(ii) Major axis perpendicular to the surface:

Area = Length of the molecule x Thickness of the aromatic ring = $7.36 \times 3.7 = 27.20$ sqA.

A value of 43 sq.A has been used in this work. This value is the same used by some previous workers at 30°C.[39]

BENZENE MOLECULE Fig.64



Area of ethyl alcohol molecule.[38] (Fig.65)

(i) Major axis parellel to the surface:

$\angle$C C O = 109.5°

C---O distance = 1.48 A

C---C distance = 1.55 A

O---H distance = 0.96 A

Van der Waals' radius for

CH_3 = 2.0 A

CH_2 = 2.0A

O = 1.4 A

x = Cos 19.5 (1.48) = 1.395 A

y = Cos 70.5 (1.48) = 0.494 A

Length of the molecule = (2.0+1.55+0.494+0.96+1.20)

= 6.204 A

Width of the molecule = (1.4+1.395+2.0) = 4.794 A

Area of the molecule = 6.204 x 4.794 = 29.76 sq.A

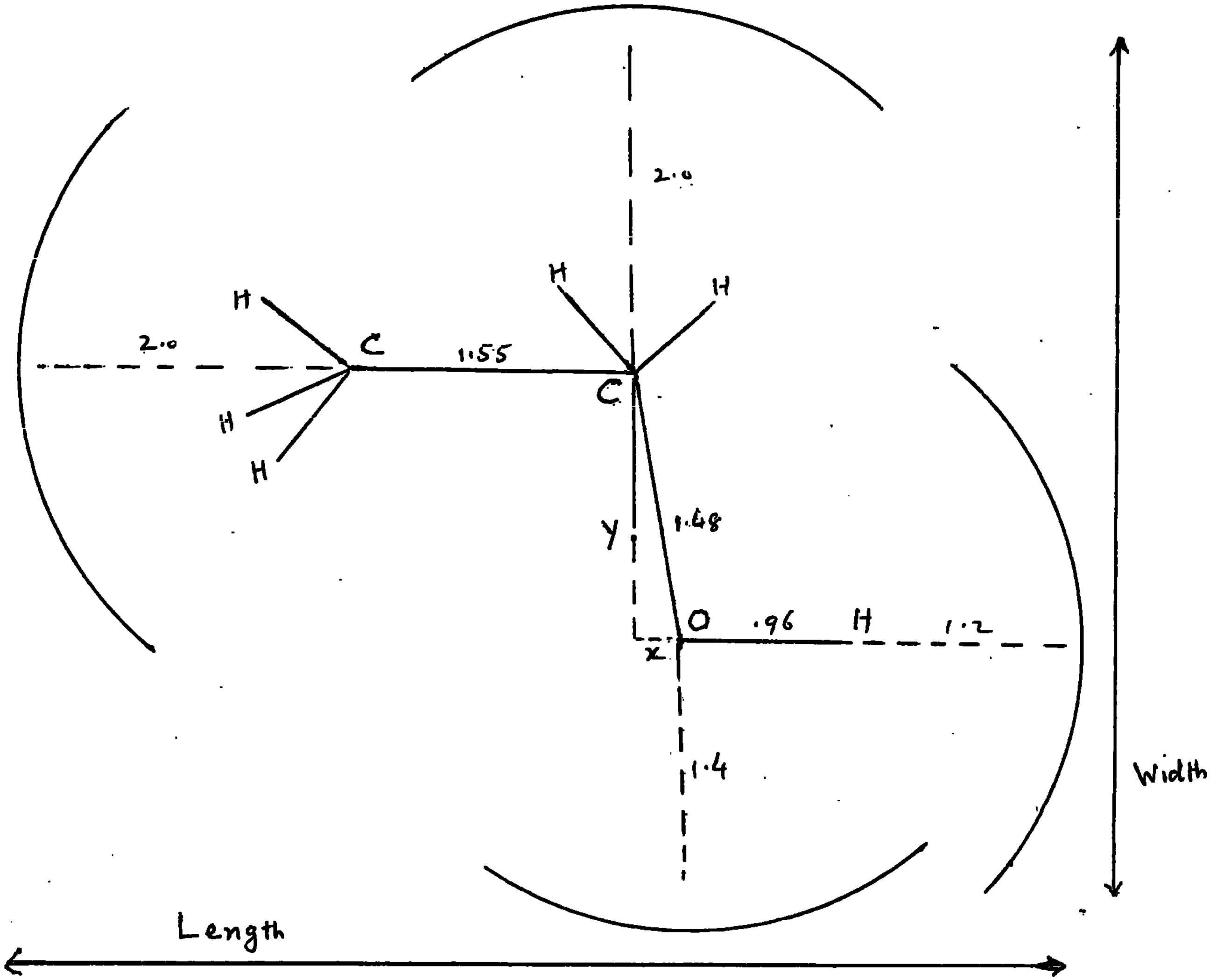
(ii) Major axis perpendicular to the surface:

Length of the molecule = 4.794 A

Width of the molecule = 4.4 A

Fig.65

ETHYL ALCOHOL



Area of the molecule = 4.794 x 4.40

= 21.50 sq.A.

A value of 21.5 sq.A has been used in this work and it is the same value as calculated above for the perpendicular orientation.

Area of the Cyclohexane molecule.[38] (Fig.67)

Major axis parallel to surface:

Van der Waals' radius for CH_2 = 2.0 A

Distance C---C =1.54 A

$\angle$C C C =110°

Distance x =1.54 (Cos 70) = 0.53 A

Distance y =1.54 (Cos 20) = 1.45 A

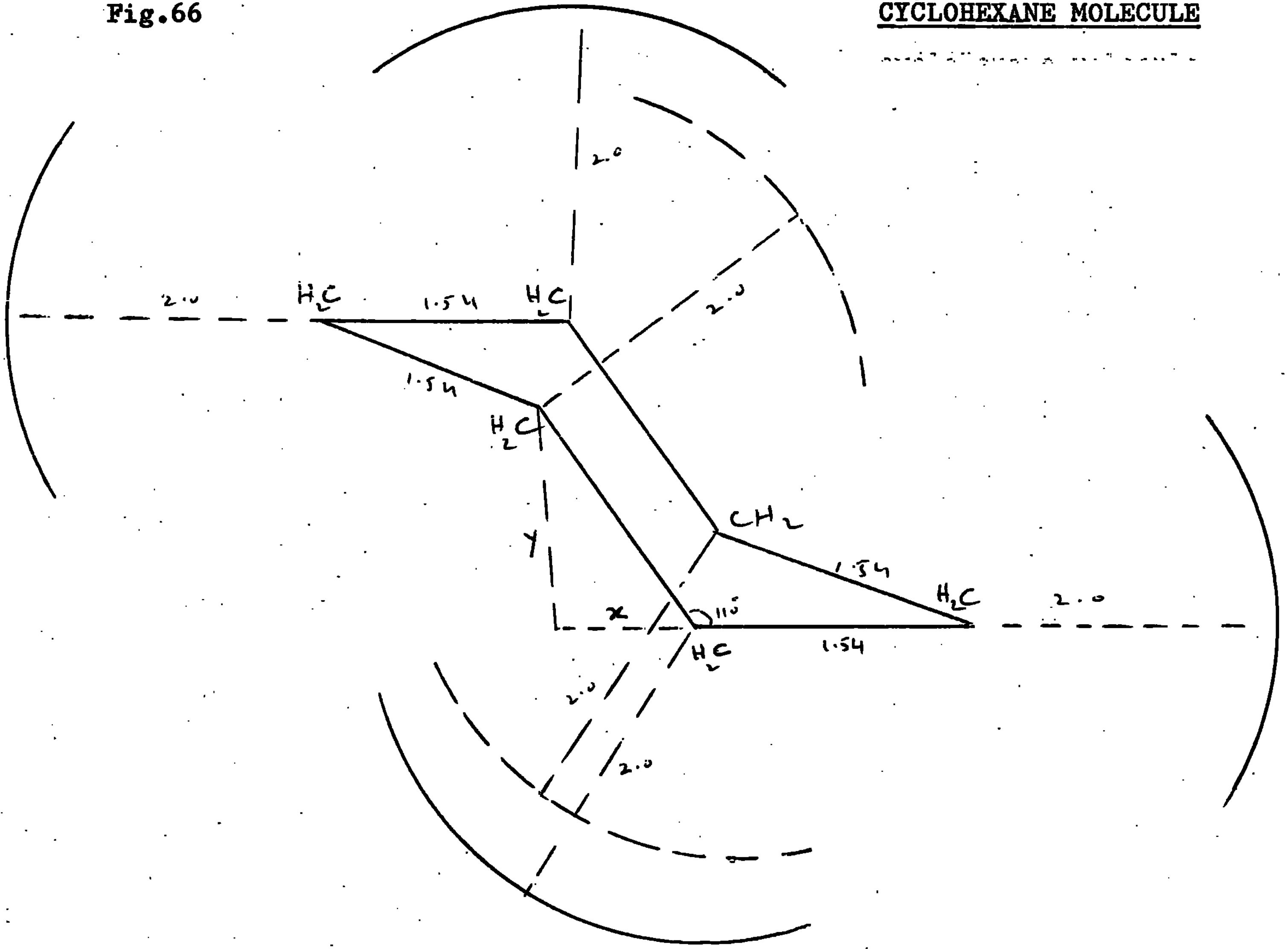
Length of the Molecule =2+1.54+0.53+1.54+2)
=7.61 A

Width of the Molecule =(2.0+1.45+1.0+2,0) = 6.45 A

Area of the Molecule =49.10 sq.A.

Fig.66

CYCLOHEXANE MOLECULE



Area for acetic acid molecule[38] (dimeric for much of the[40] concentration range in benzene, cyclohexane and CCl_4).

Major axis parallel to surface: (Fig.67)

Distance C--C = 1.54 A

Distance C--O = 1.43 A

Distance C--O', = 1.24 A

Distance O'--O = 2.67 A

$\angle$O C O = 130°

x = 1.43 Sin 65 = 0.906 (1.43) = 1.296 A

y = 1.24 Sin 65 = 0.906 (1.24) = 1.124 A

z = 1.34· (0.4226)=0.566 A

Width of the molecule = 1.4+1.4+1.124+1.296 = 5.22A

Half length = (2.0+1.54+0.56+0.566+2.67+1.54+2)

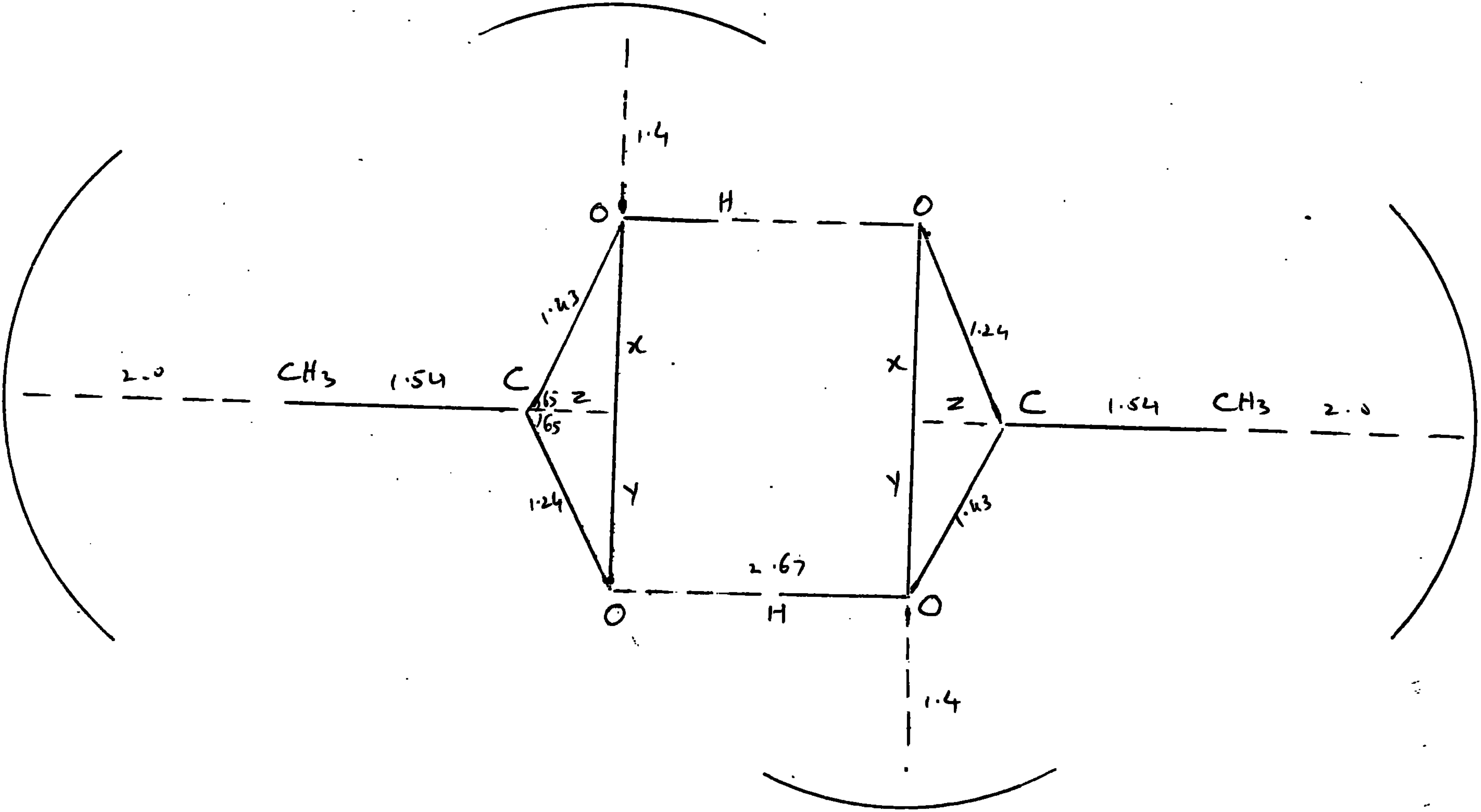
= 5.44A

Area of the molecule = 5.44 x 5.22 = 28.10 sq.A.

The above calculated vaue of 28.1 sq.A has been used as the molecular area of acetic acid molecule with major axis parallel to surface.

Fig.67

ACETIC ACID MOLECULE (Dimeric)



Area of the Propionic Acid Molecule. (Fig.68)

Major axis parallel to surface:

Van der Waals' radius for CH_3 = 2.0 A

" " " " for Oxygen = 1.4 A

Distance C---C = 1.54 A

Distance C---O = 1.43 A

Distance $C---O'$ = 1.24 A

Distance $O'---O$ = 2.67 A

$\angle O\ C\ O = 130^\circ$

Length of the molecule = (2.0+1.23+1.23+0.56+2.67+0.56 + 1.23+1.23+2.0)

=6.35 A

Width of the molecule = (1.4+1.12+1.296+1.4)

= 5.22 A

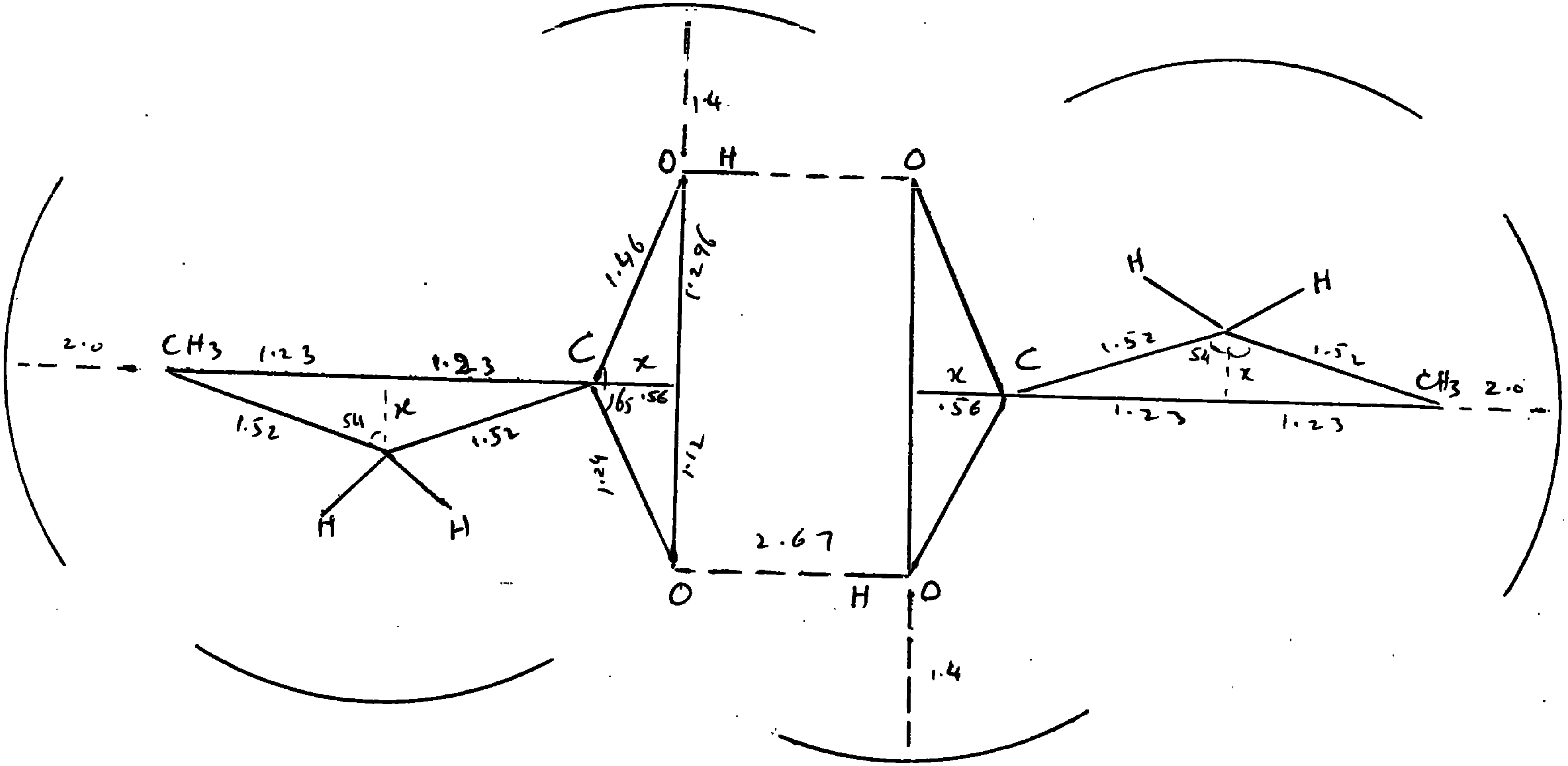
Area of the molecule = 6.35 x 5.22

= 33.11 sq.A.

The above calculated value of 33.1 sq.A has been used as the molecular area of propionic acid molecule with major axis parallel to the surface.

Fig.68

PROPIONIC ACID MOLECULE (Dimeric)



Area of butyric acid molecule. (Fig.69)

Major axis of the molecule parallel to the surface:

Van der Waals' radius for CH_3 = 2 A

" " " " for Oxygen = 1.4 A

Distance C---O = 1.43 A

Distance C---C = 1.54 A

Distance O'---O = 2.67 A

$\angle$O C.O = 130°

Length of the molecule = (2.0+1.22+1.23+1.23+0.56+1.34)

= 7.59 A

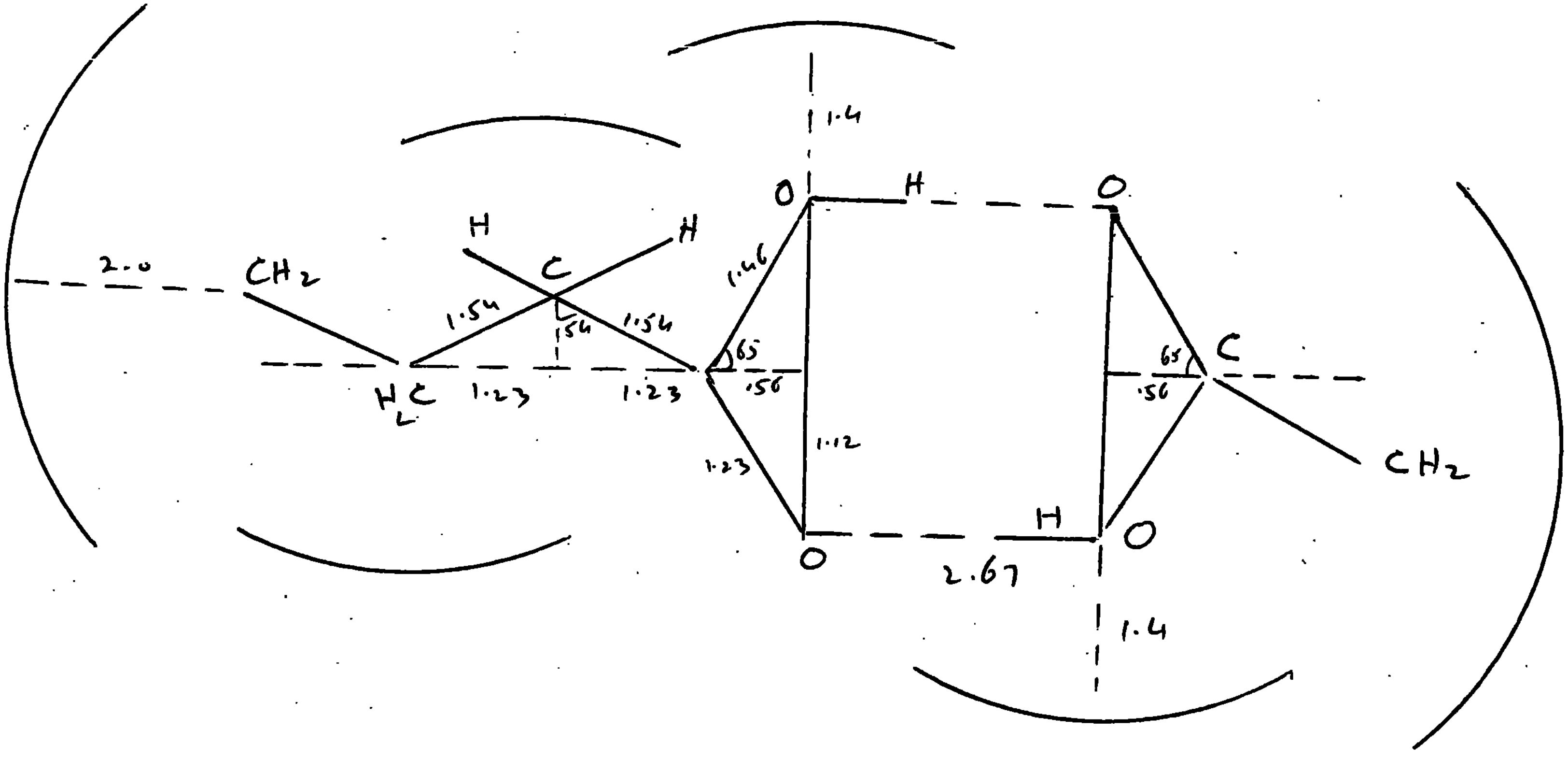
Width of the molecule = (1.4+1.12+1.296+1.4)

= 5.22 A

Area of the molecule = 7.59 x 5.22

= 39.50 sq.A.

Fig.69 **BUTYRIC ACID** (parallel orientation)



CHAPTER 10.

Vapour Pressure - Composition Curves: Affinities between Components in the liquid phase.

In the study of liquid mixtures it is convenient to define an ideal solution as one obeying Raoults' law over the whole range of concentration. Suppose Raoults' law, (that the partial vapour pressure of a constituent is proportional to its mole fraction in the liquid at all compositions) applies to A then

$$P_A = P^o_A x_A$$

Similarly if we consider the other constituent B,

then $P_B = P^o_B x_B$.

Here P is partial vapour pressure of any constituent and x is its mole fraction; P^o indicates vapour pressure of the pure component. If a mixture of two liquids behaves ideally, then according to the above equations the plot of the partial pressure of each constituent against its mole fraction in the liquid phase should be a straight line passing through the origin, and the total vapour pressure of the system $P_T (= P_A + P_B)$ also varies linearly with concentration.

If the two components of a mixture differ in (i) internal pressure (ii) polarity (iii) length of hydrocarbon chain or analogous grouping or if (iv) one or other of the components is associated in the liquid state, the system does not behave ideally; the four factors mentioned all result in positive deviations from Raoults' law. If the two constituents of a mixture are such that the molecules of A and B attract each another strongly and particularly if there is partial compound formation between A and B in the liquid phase, the vapour pressure of each constituent may be less than that required by Raoults' law. Such a system can, therefore, exhibit negative deviations from ideal behaviour.

It is pertinent to the question of the ease with which one component can escape from the environment of the other component in a binary solution to examine the behaviour of the vapour pressure curves of the various systems.

1. <u>Benzene.</u> The vapour-pressure curves for acetic acid + benzene, propionic acid + benzene and butyric acid +

benzene systems are shown in Figs. 2, 7 & 12. The positive deviation from Raoults' law decreases with increasing acid chain length. This indicates that the affinity between acetic acid and benzene molecules, in the liquid phase, is weak, and increases with increasing chain length. The curve for butyric acid + benzene system shows the two components behave almost ideally, and the positive deviation is quite small.

2. Carbon Tetrachloride. Figs. 3, 8 & 13 show the vapour pressure curves for acetic, propionic and butyric acids in carbon tetrachloride, respectively. Again, the positive deviation from Raoults' law decreases with increasing acid chain length. This shows that the affinity between acetic acid and carbon tetrachloride molecules is small and increases with increasing chain length of acid. The vapour-pressure curve for butyric acid + carbon tetrachloride shows only a small positive deviation, and this system behaves almost ideally.

3. Cyclohexane. The vapour-pressure curves for acetic propionic and butyric acids in cyclohexane systems are

shown in figs. 4, 9 & 14 respectively. Marked positive deviation is shown by all the three systems, but the positive deviation decreases with increasing acid chain length. This indicates that the affinity between the components in the liquid phase is least in the acetic acid + cyclohexane system, and increases with increasing chain length of acid.

4. Ethyl alcohol. The vapour-pressure curves for the system acetic acid + alcohol and propionic acid + alcohol are shown in figs 5 & 10. The deviation from Raoults' law is negative for both the systems; however, it is more negative for the first system. Hence the affinity between acetic acid and alcohol is more than that between propionic acid and alcohol in the liquid phase. For ~~in~~ these systems the affinities decrease with increasing chain length of acid.

5. Water. Figs.6, 11 & 15 represent the vapour-pressure curves for acetic, propionic and butyric acids in water, respectively. Positive deviation is highest for the butyric acid + water system and decreases as the acid chain length

gets shorter. However, it is almost linear, but slightly negative in the case of acetic acid, and suggests a relatively strong affinity between acetic acid and water. Thus for these systems the affinities between the two components decrease with the increasing chain length of acid.

CHAPTER 11.

Surface Tension Changes at the Liquid-Vapour Interface.

The relationship between adsorption and surface tension was first derived by Gibbs (1878) and is known as the Gibbs adsorption equation. As a result of the tendency of the free energy of a surface to decrease, the concentration of a solute on the surface may differ from that in the bulk of the solution. The component with the lower surface tension will tend to concentrate in the surface, for in this way the free energy of the system is reduced. It follows, therefore, from general considerations, that if a solute lowers the surface tension at a given interface, there will be a greater proportion of solute to solvent at the interface than in the bulk of the solution. This will consequently represent a case of adsorption of the solute at the surface of the solution. On the other hand, if the solute brings about an increase of surface tension, its concentration at the surface will be less than in the bulk of the solution, and hence a negative adsorption of solute will result.

A combination of the factors associated with the effect on surface tension of adding acid to acid a+d solvent mixtures as well as affinity between acid and solvent in the liquid phase (already discussed in chapter 10) is relevant to a proper understanding of surface excess values at the liquid-vapour interface.

The surface tension of all the systems at various concentrations have been measured. The effect of adding acid to solution of acid + solvent for all the systems will now be discussed.

1. Benzene. (Table-43, 48 & 53). The surface tension values of acetic acid + benzene system, at various concentrations, show that, at first, increase of acid content lowers the surface tension of the solution; this lowering continues up to the value of 0.5 mole fraction of acid where a minimum value of 25.6 dynes/cm., approximately, is obtained. After this further addition of acid results in an increase in the surface tension values. In the case of propionic acid and butyric acid it is noted that increase of acid content in the respective solutions results in a continuous decrease in surface tension values of the solutions. For these systems, the

rate of decrease of surface tension of the solutions with acid addition increases with increasing chain length of acid.

2. <u>Carbon tetrachloride.</u> (Table-44, 49 & 54). The values of surface tension of solutions of acetic acid, propionic acid and butyric acid separately in carbon tetrachloride show that a lowering of surface tension with added acid occurs for a certain range of concentration in each case after which further increase of acid concentration causes a gradual increase in the surface tension values. It is further noted that the rate of lowering of surface tension values, (over the concentration range for which this is the case), on the addition of acid increases with increasing acid chain length.

3. <u>Cyclohexane.</u> (Table 45, 50 & 55). The surface tension of acetic acid + cyclohexane solutions decreases gradually with increasing acid concentration for a certain concentration range, but subsequently further increase of acid concentration results in a sharp increase of the surface tension of the solution. In the case of propionic and butyric acids, it is

noted that the addition of acid results in an increase in the values of surface tensions of the solutions over the whole concentration range.

When the effect of adding acid to the corresponding solutions for the three acids is considered, it is noted that the "lowering" of surface tension decreases with the increasing acid chain length.

4. Ethyl Alcohol. (Table 46 & 51). The surface tension values of solutions of acetic and propionic acids in alcohol at various concentrations of the acids show that increase of acid concentration increases the surface tension of the solutions. It is also noted that the rate of increase of surface tension of acid + alcohol solution increases in going from acetic acid to propionic acid.

5. Water. (Table 47, 52 & 56). The surface tension values of solutions of acetic, propionic and butyric acids in water, at various concentrations, are lowered by the addition of acid to the solutions, throughout the whole concentration range. This lowering of surface tension of solutions of acid + water, at different concentrations, increases in its rate with increasing acid chain length.

CHAPTER 12.

Individual Isotherms.

The resolution of the composite isotherms into the individual isotherms is of great help in the study of the nature of interfaces. Equations (36) and (47) have been used to resolve the composite isotherms obtained in this work into the individual isotherms. It is generally assumed, throughout the present discussion that the thickness of the adsorbed layer is unimolecular. This assumption has been supported, in general, by experimental investigations of several previous workers, e.g. Guggenhiem and Adam[7], Harkins and Wampler[4], and Aveyard[27]. Direct evidence for this assumption is difficult to obtain, but it seems to be generally accepted because it gives results compatible with values of Γ calculated from the Gibbs equation. Moreover the values of Γ are, for almost all the systems, very much smaller than would be required to satisfy the assumption of multilayer adsorption.

It is believed that the three acids are essentially dimeric in benzene, carbon tetrachloride and cyclohexane mixtures. This is supported by Harris and Hobbs[40] and some other workers. The acids appear to show a momomeric behaviour in alcohol and water.[41,42] The acid molecules are believed to be associated intermolecularly with alcohol or water molecules.

Both parallel and perpendicular orientations of the molecules of different components, in all the sustems, are considered in the calculations but it appears likely that the most probable orientations of the three acids at the interface for solution of benzene, carbon tetrachloride and cyclohexane are the ones in which the molecules of the constituents are oriented parallel to the surface.

The parallel orientation of the three acids used in non-polar solvents is readily understood because the acids are largely dimersed in such solvents. In this type of orientation the double hydrogen bonding between the carboxyl gruops of the dimer is preserved on adsorption. When the second component (solvent) is non-polar, no strong bond between acid and solvent can be formed to compensate for the rupture of the hydrogen bonds in the dimeric acid molecule. This orientation is indeed supported by the work of different investigators.[5, 27, 43] Acid dimers do not appear to be present in water and alcohol solutions. The most probable orientation of the three acids in the above two solvents is considered to be the one in which the molecules are essentially perpendicular to the surface. With this orientation association by hydrogen-bonding between acid and solvent can occur in the adsorbed phase (as already exists in the bulk solution), although the extent of association between acid and solvent in bulk solution and at the interface need not be the same. This type of orientation of water and alcohol molecules is supported by Guggenhiem and Adam[7], and by Cornford, Kipling and Wright.[23]

<u>(A) Acetic Acid Systems.</u>

1. <u>Benzene.</u> The individual isotherms of acetic acid and benzene are shown in fig.44. The most probable orientations of the acid and benzene are the ones, as discussed before, in which the molecules of both the constituents are oriented parallel to the surface. This orientation requires 43 sq.A. as the molecular area for a benzene molecule and 28 sq.A. for a single acid molecule.

The amount of benzene is greater than that of the acid at the interface at the lower concentrations of acid in the liquid phase, but with increasing acid concentration in the liquid phase the amount of acid at the interface increases whereas that of benzene decreases. Eventually the amount of acid at the interface becomes greater than that of benzene. It is clear from the isotherms that a complete monolayer of acid is formed only from the pure acid.

It is noted that the adsorption of the acids at the interface, with benzene as solvent, increases with increasing acid chain length. The vapour pressure curves for the corresponding systems show that the positive deviation from Raoults' law decreases with increasing chain length, indicating increasing affinity between acid and benzene, in the liquid phase, with increasing chain length. So this factor is not the dominant one in the observation of increasing adsorption with increasing chain length. Now the second factor, relatively greater decrease in surface tension values with the increasing acid chain length may be considered. It follows from general considerations, that if a solute lowers the surface tension at an interface, there will be a greater proportion of solute to solvent at the interface, and if the rate of lowering increases with increasing chain length, then the amount of acid may be reasonably expected to increase accordingly in these systems. Hence in the systems under discussion it is suggested that the relative greater lowering of surface tension in the three systems is the factor which is dominant over the affinity factor, and results in increasing adsorption with increasing chain length.

2. Carbon Tetrachloride. The individual isotherms for acetic acid and carbon tetrachloride are shown in fig.45. The solvent molecule is almost spherical in shape and has a calculated area of 45 sq.A. The molecular area for acid is taken as 28 sq.A. The most probable orientation of acid and solvent molecules is the one in which the molecules are oriented parallel to the surface.

The amount of the acid at the interface increases as the acid concentration in the liquid phase increases and it is high at high concentrations of the acid in the liquid phase. A mixed monolayer over the whole concentration range is noted and a complete monolayer of acid is formed only from pure acid.

The number of moles of solute in the interface at any concentration is lower than those for the other two acids. The vapour-pressure curves show the greatest positive deviation, which, as discussed, indicates weak affinity between the constituents in the liquid phase and hence greater escaping tendency of acid from solution. So this factor does not support the above increasing adsorption of acid with increasing acid chain length. On the other hand it is noted that the rate of lowering of surface tension is less in this system than the other two systems. This supports less adsorption of acid at the interface than for the other two acids. So this latter factor would account for the observed adsorption in this system as compared with other two corresponding systems.

3. <u>Cyclohexane.</u> The individual isotherms of acetic acid and cyclohexane are shown in fig.46. The most probable orientations of the solute and solvent molecules are considered to be the ones in which the molecules lie parallel to the surface, as already discussed before. This orientation requires 48 sq.A. and 28 sq.A. as the molecular areas of cyclohexane and acetic acid, respectively.

The number of moles of acid per unit area of the surface is small at the lower concentrations of the acid in the liquid phase but it increases with increasing concentration. Eventually the amount of acid becomes greater than that of the solvent. A complete monolayer of acid is formed only from the pure acid.

It is noted that the adsorption of acid is more in this system than the corresponding propionic and butyric acid systems. The vapour-pressure curve for this system shows very large positive deviations from Raoults' law, and also much greater than the ones shown by corresponding propionic and butyric acid systems. This means that the affinity between acetic acid and cyclohexane in the liquid phase is much less than that between the constituents of other two corresponding systems. The escaping tendency of the acetic acid from the solution is thus much greater than for the other two acids and this appears to be the dominant factor controlling the amount of adsorption in this system.

4. Ethyl alcohol. Fig.61 represents the individual isotherms of acetic acid and ethanol. The most probable orientations of acid and alcohol molecules are considered to be the ones in which the major axes of the molecules

are perpendicular to the surface. This orientation seems likely by the fact that the polar-OH group of alcohol can be attracted strongly by the polar carboxyl group of acid, so that a strong interaction between these polar groups at the interface is possible. The area per molecule of alcohol is taken as 22 sq.A while that of acid is taken as 25.8 sq.A.

The amount of acid in the interface is low at lower concentrations of the acid in the liquid phase but increases with increasing acid concentration in the liquid phase. The overall situation at the interface is that the amount of alcohol is more than that of the acid for more than fifty percent of the concentration range. A complete monolayer of acid is formed only from the pure acid.

It has been noted from the surface tension measurements that the addition of acid increased the surface tension of the acetic acid + alcohol mixtures. Hence according to general rule, the acid should show a negative adsorption, as it does (shown by the composite isotherm), which means preferential adsorption of the alcohol.

Secondly the negative deviation of the vapour-pressure curves for this system shows that the affinity between the acid and alcohol is very strong in the liquid phase and hence the escaping tendency of acid from the liquid phase will be low. This will also tend to reduce acid adsorption. Hence both the factors discussed here tend to favour preferential adsorption of alcohol.

5. Water. The individual isotherms for acetic acid and water are shown in fig.48. The most probable orientation of the acid is considered to be the one in which the molecules lie perpendicular to the surface. This orientation, as suggested before, is supported by the fact that the ploar groups of the two components attract each other strongly. The molecular area for ~~which~~ water is taken as 10 sq.A and 25.8 sq.A for acetic acid.

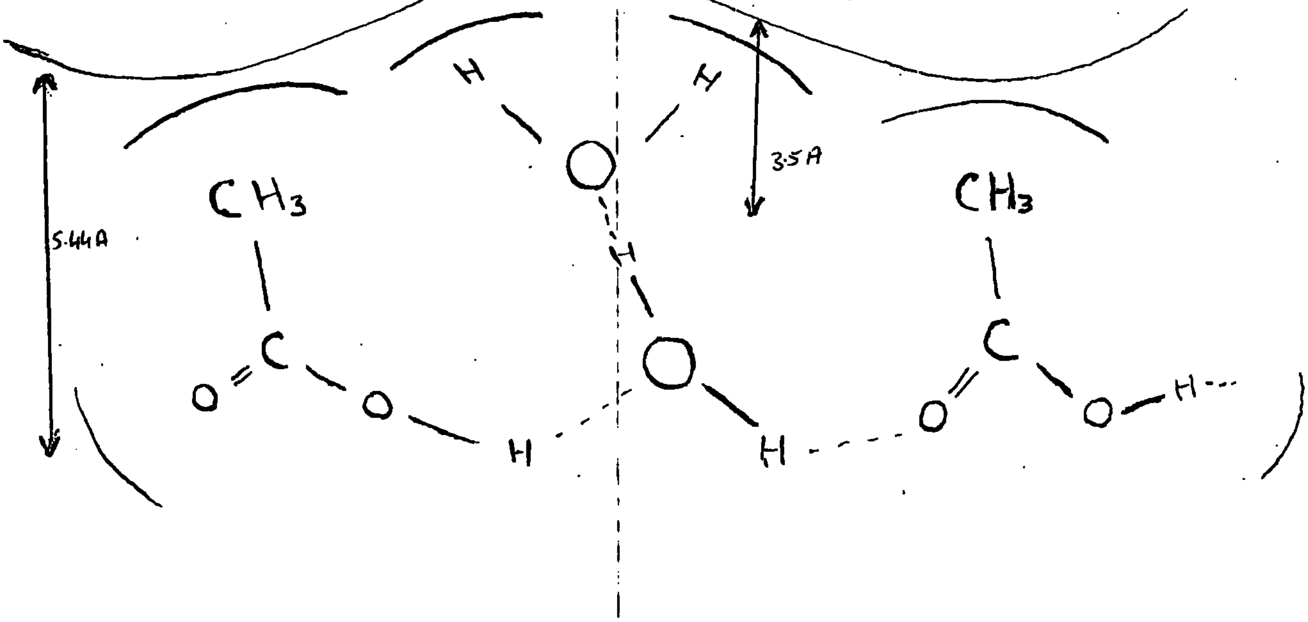
The isotherms show that the number of moles of water at the interface is very high at very low concentrations of acid in the liquid phase. One of the reasons for this may be the smaller area of water molecules than those of the acid molecules and hence a greater number of moles is required to cover a given area. However the overall position of the surface, as is clear from the isotherms, is that there is more acid than water for much of the concentration range. A complete monolayer of acid however is only obtained from the pure acid.

The adsorption of acid at the interface increases with increasing acid chain length. The vapour-pressure curves show that the positive deviation decreases with decreasing acid chain length, thus the affinity between acid and water, in the liquid phase should decrease with increasing chain length. So this factor supports the increasing adsorption of acid with increasing chain length. The lower adsorption of acetic acid at the interface (than for propionic and butyric acids) is also concordant with the fact that the rate of lowering of surface tension of acid-water mixtures with the addition of acid to the liquid phase, increases with increasing acid chain length. This has already been discussed in chapter 10.

The distinction between monolayer and multilayer of adsorption cannot be made rigidly in many cases. It can only be applied precisely to systems in which the molecules of the two components have the same thickness at the surface. Few systems fulfil this criterion exactly, though many which have been investigated do so to a close degree of approximation.

The water molecule is smaller in size than that of acetic acid and it seems likely that more than one molecule will be required for the length of acid. It is suggested that two water molecules are present along the length of the acid molecule which is believed to be perpendicular to the surface for this system. In this system the fraction of surface covered by the acid, at the acid concentration where the two individual isotherms cross each other, is almost the same calculated from the model indicated below:

Solution-Vapour Interface



Propionic acid systems.

1. Benzene. The individual isotherms of propionic acid and benzene are shown in fig.49. The most probable orientations of the acid and benzene, as for the corresponding acetic acid system, are the ones in which the molecules of both the constituents are oriented parallel to the surface. The calculated molecular areas are 43 sq.A for benzene and 33 sq.A for the acid.

The individual isotherms reveal that the number of moles of the acid per unit area of the surface is quite low at the lower concentrations of acid in the liquid phase but this amount increases with the increasing acid concentration, whereas that of benxene decreases. Eventually the amount of acid at the interface becomes greater than that of benzene. A complete monolayer of acid is formed only from the pure acid.

The vapour Pressure curves show that positive deviation from Raoults' law is smaller than the one shown by corresponding acetic acid system. Thus the affinity between acid and benzene in the liquid phase is expected to be greater than that of acetic acid and hence less adsorption of propionic acid at the interface should result if this were the dominant factors controlling adsorption. But it is noted that the preferential adsorption of propionic acid at the interface is more than that of acetic acid. This could be explained by the fact that a larger lowering of surface tension takes place in this system than in acetic acid + benzene system when acid is added to the solutions, and hence more adsorption of propionic acid results at the interface. This has been discussed in detail in the corresponding acetic acid system.

2. Carbon tetrachloride. The individual isotherms for the system propionic acid + carbon tetrachloride are shown in fig.50. The most probable orientation of the acid is considered to be the one in which the acid molecules lie parallel to the surface, just as for the corresponding acetic acid system. This requires an area of 33 sq.A for the single acid molecule.

The isotherms show that preferential adsorption of acid is low at the lower concentrations of acid in the liquid phase but it increases with the increasing acid concentration in the liquid phase and eventually the amount of acid at the interface becomes greater than that of carbon tetrachloride. A complete monolayer of acid is only formed from pure acid.

The adsorption of propionic acid at the interface is greater than that of acetic acid for the corresponding system. This shows that preferential adsorption of acid increases with the increasing acid chain length. The affinity between the acid and the solvent, as shown by the vapour pressure curves, increases with increasing acid chain length. This would tend to cause a decrease in adsorption with increasing acid chain length. So this factor does not help in explaining the above fact. On the other hand it is noted that relative lowering of surface tension of acid + carbon tetrachloride mixtures, increases with increasing acid chain length. Hence this factor is dominant over the affinity factor in affecting adsorption from carbon tetrachloride and results in increase of acid adsorption at the interface, with increasing acid chain length.

3. Cyclohexane. Fig.51 shows the individual isotherms of propionic acid and cyclohexane. The most probable orientation of the acid and cyclohexane molecules is considered to be the one in which the molecules lie parallel to the surface, just as for the corresponding

acetic acid system. This orientation requires 33 sq.A for the molecular area of the acid and 48 sq.A for the molecular area of cyclohexane. It is clear from the individual isotherms that a complete monolayer of acid is formed only from the pure acid. In this system it is noted that the adsorption of acid is lower than the adsorption of acid in the corresponding acetic acid system at similar concentrations. This fact can be understood by the behaviour of the vapour pressure curves which show decreasing positive deviation with increasing acid chain length and hence increasing affinity between the solute and solvent in the liquid phase. So the affinity between propionic acid and cyclohexane is greater than that between acetic acid and cyclohexane. Decrease in acid adsorption with the increasing acid chain length is again supported by the fact that the relative lowering of the surface tension is found to be decreasing with increasing acid chain length.

4. Ethyl alcohol. The individual isotherms for the system propionic acid and ethanol are represented in fig. 52. The perpendicular orientation for both the acid and alcohol molecules, as for the corresponding acetic acid

system, is considered to be the most probable orientation. The area used for the alcohol molecule is 22 sq.A and that for the acid molecule is taken as 20.5 sq.A.

The number of moles of acid per unit area of the surface is small at the lower concentrations of acid in the liquid phase, but this increases with increasing acid concentration in the liquid phase. There is more alcohol than acid at the interface over a larger concentration range and a monolayer of acid is formed only from the pure acid.

Preferential adsorption of alcohol is greater for this system than for the corresponding acetic acid system. This can be understood by the fact that increase in surface tension of acid + alcohol mixtures, on the addition of acid in the liquid phase increases with increasing acid chain length. The decreasing affinity between the two components, in the liquid phase, with increasing acid chain length which would be expected to result in increasing adsorption of acid with increasing chain length, does not appear to be the dominant factor controlling adsorption in this system.

5. Water. The individual isotherms for the propionic acid and water system are shown in fig.53. The most probable orientation of the acid is considered to be the one in which the acid molecules are oriented perpendicular to the surface layer and hydrogen-bonded in chains to water molecules or to other acid molecules. The molecular area for water is taken as 10 sq.A while that of the acid is taken as 20.5 sq.A.

The isotherms reveal that the number of moles of the water at the interface is very high at very low concentrations of acid in the liquid phase. This may be due to the small area of water molecule which requires a greater number of moles to cover a given area. The amount of acid increases at the interface with increasing acid concentration and eventually at a relatively low bulk acid concentration this amount at the interface becomes greater than that of water. However, a complete monolayer of acid is obtained from the pure acid.

Preferential adsorption of the acid is more in this system than in the corresponding acetic acid system. This is concordant with the observations that the affinities between the two components in the liquid phase decrease with increasing acid chain length, and also that the lowering of surface tension of acid-water mixtures by addition of acid increases with increasing acid chain length.

Butyric acid systems.

1. Benzene. The individual isotherms for the system butyric acid and benzene are shown in fig.54. The most probable orientations of the solute and solvent molecules are considered to be the ones in which the molecules are oriented parallel to the surface, as for the corresponding acetic and propionic acid systems. The molecular areas of acid and benzene are taken as 38 sq.A and 43 sq.A, respectively.

The number of moles of the acid per unit area of the surface is small at the lower concentrations of the acid in the liquid phase but increases with increasing acid concentrations. Eventually the amount of acid at the interface becomes greater than that of benzene. A complete monolayer of acid is formed only from the pure acid.

The amount of acid adsorbed at the interface is greater than the amounts adsorbed for the corresponding propionic and acetic acid systems at similar acid concentrations in the bulk. The vapour pressure curves reveal the least positive deviations in this system, which indicates more affinity between the constituents in the liquid phase. This would tend to decrease adsorption of acid from this system, and hence this factor does not appear to be the dominant one controlling adsorption in this case. On the other hand it is noted that relative lowering of surface tension is the greatest in this system, and hence it is suggested that this factor is the adsorption - controlling factor, resulting in greater preferential adsorption of butyric acid than of acetic and propionic acids at the interface.

2. <u>Carbon tetrachloride.</u> Fig. 55 shows the individual

isotherms for the system butyric acid + carbon tetrachloride. The most probable orientation of the acid is considered to be the one in which the molecules lie with their major axes parallel to the surface, thus giving an area of 38 sq.A for butyric acid molecule. The molecular area of carbon tetrachloride is taken to be the same as in the corresponding systems with the other acids.

The adsorption of the acid is low at the lower concentrations of the acid in the liquid phase but increases with increasing acid concentration. A mixed monolayer is noted over the whole concentration range, and a uni-monolayer of acid is formed only from pure acid.

Preferential adsorption of acid at the interface is greater than that of acetic and propionic acids at similar concentrations in the corresponding systems. From the vapour pressure curves the acids show less possitive deviations with increasing acid chain length, so this factor cannot be used to explain the above fact satisfactorily, because affinity between the components in the liquid phase increases with increasing acid chain length; this would be expected to result in decreasing adsorption with increasing acid chain length. The second factor, relative greater decrease of surface tension with increasing acid chain length as acid is added to acid + solvent mixtures, favours increasing preferential adsorption of acid with increasing acid chain length.

3. Cyclohexane. The individual isotherms for the system butyric acid + cyclohexane are shown in fig.56. The most probable orientation of the acid and cyclohexane molecules is assumed to be the same as in the case of corresponding propionic acid system. The molecular areas are 38 sq.A for butyric acid and 48 sq.A for cyclohexane. A complete monolayer of acid is formed only from the pure acid.

The adsorption of butyric acid, as compared with other two acids in the corresponding systems for similar concentrations, is the least in this system. The affinity between the components in the liquid phase, as shown by the vapour pressure curves, is maximum in this system. Hence butyric acid has a lower escaping tendency from the solution than the other acids, and this results in a lower preferential adsorption of the acid. Also the relative lowering of surface tension is found to decrease with increasing acid chain length, again favouring decreasing adsorption of acid with increasing chain length.

4. Water. Fig.57 shows the individual isotherms for butyric acid and water. The most probable orientation of acid is assumed to be the same as for acetic and propionic acid systems. The area per molecule of butyric acid is taken as 20.5 sq.A and that for water, 10 sq.A.

The isotherms reveal that the number of moles of water at the interface is very high for very low acid concentrations in the liquid phase. This may be due to the small area of water molecule which requires a greater number of moles to cover a given area. The amount of acid at the interface increases steeply at first with increasing acid concentration in the liquid phase and eventually this amount of acid becomes greater than that of water. A complete monolayer of acid is formed only from the pure component.

It is noted that preferential acid adsorption increases with increasing acid chain length. This can be understood in terms of both by the affinity as well as relative lowering of surface tension factors. The affinities between the components in thd liquid phase, as shown by the vapour-pressure curves, decrease with increasing acid chain length. Also the relative lowering of surface tension as acid is added to acid + water mixtures increases with increasing acid chain length. Both the above factors thus favour increasing ~~in~~ acid adsorption at the interface with increasing acid chain length.

CHAPTER 13.

Variation in Nature of the Interface with Solvent.

(a) Acetic acid system. The fractions of surface covered by acetic acid at different concentrations in the liquid phase for solutions with the different solvents are represented in fig.58. It is noted that the fraction of the interface covered by acid increases for each solvent, with increasing concentration of acid in the liquid, phase.

The preferential adsorption of acetic acid at the interface is very high in water and decreases in the order of water, benzene, carbon tetrachloride, cyclohexane and alcohol.

The vapour pressure curves for acetic acid + benzene, acetic acid + carbon tetrachloride and acetic acid + cyclohexane systems show positive deviations, while those for acetic acid + alcohol and acetic acid + water systems show small negative deviations from Raoults' law. This indicates that the affinity between the components in the liquid phase, in the first three systems, is lower than for the last two systems. Therefore the amount of acid adsorbed should be more in the first three systems than the last two systems. So this factor cannot be used to explain satisfactorily the order of adsorption of acid in all the systems. It is noted from the vapour pressure curves that positive deviation is small in the acid + benzene system, is larger in the acid + carbon tetrachloride system and is even greater still in the acid + cyclohexane system. This shows that the affinity in the liquid phase between the components in the above three systems decreases accordingly. Thus increasing acid adsorption may be expected in this order for the above three systems if this were the adsorption controlling factors. This, however is not the order of adsorption observed.

Relative lowering of surface tension of acid + water mixtures, on the addition of acid, is highest, as compared with the other systems. Thus the greatest adsorption of acid from this system is in accord with this. For the other systems, the relative lowering of surface tension decreases from benzene to cyclohexane and in alcohol +

acid system, the addition of acid to acid + alcohol solutions increases the surface tension. Hence the rate of lowering of surface tension decreases in the order of water, benzene, carbon tetrachloride, cyclohexane and alcohol, which is also the observed order of decreasing adsorption of acid.

The most probable orientation of acid and water as discussed before is considered to be the one in which molecules are perpendicular to the surface and thus the highest value of acid adsorption in this system can also be favoured by the fact that the -OH group attracts the polar -COOH group of the acid. This orientation of the molecules favours the possibility of a strong interaction between the polar groups at the interface. In the three non-polar solvents (cyclohexane, carbon tetrachloride and benzene) the acid molecules are believed to be essentially dimeric, and the orientation of both molecules in each of the three systems appears to be that for which the major axes of the molecules are parallel to the surface.

(b) <u>Propionic acid systems.</u> The fractions of surface covered by propionic acid with the various solvents at different concentrations in the liquid phase are represented in fig.59. It is noted that the fraction of the surface covered by acid increases, for each solvent, with increasing acid concentration in the liquid phase.

The order of fraction of surface covered by acid for the various solvents is the same as for acetic acid, i.e., water, benzene, carbon tetrachloride, cyclohexane and alcohol.

The vapour pressure curves show positive deviation for acid + benzene, acid + carbon tetrachloride, acid + cyclohexane and acid + water systems, a slight negative deviation from Raoults' law is only shown by acid + alcohol system. This indicates that the affinities between the components in the liquid phase are lower in the first four systems than in the acid + alcohol system. Thus more adsorption of acid may be expected from the four systems than from the last system. This can be used to account for the smallest adsorption of acid from acid + alcohol mixtures. As for as the order of adsorption of acids in the other solvents is concerned it is noted that the affinity factor does not account for this satisfactorily, because the relative adsorption of acid in the first three systems would then be expected to be highest in the cyclohexane system.

The relative lowering of surface tension of acid + water mixtures, on the addition of acid in the liquid phase is highest when compared with the other systems. This suggests high values of acid adsorption in this system and hence the maximum fraction of surface covered by acid in this system is strongly understood. For the other systems relative lowering of surface tension decreases from benzene to cyclohexane and in the case of acid + alcohol systems, the addition of acid increases the surface tension.

Thus the rate of lowering of surface tension is found to decrease in the order of water, benzene, carbon tetrachloride, cyclohexane and alcohol, which is also the observed order of decreasing preferential adsorption of propionic acid. So it is suggested that relative lowering of surface tension of acid + solvent mixtures on acid addition accounts for the order of adsorption of the acid in the five solvents.

It is suggested, in the case of the acid + water system, that the polar-OH group of water attracts the polar -COOH group of the acid at the interface. Perpendicular orientation of the acid at thesurface favours the possibility of a strong interaction between the polar groups at the interface. A similar type of orientation is favoured too for the alcohol system, but in this case, preferential adsorption of alcohol rather than of acid, is the observed occurrence.

(c) <u>Butyric acid systems.</u> Fig.60 represents the fraction of surface covered by butyric acid at different acid concentrations in the liquid phase for the different solvents used. The fraction of surface covered by acid increases with increasing acid concentration in the liquid phase in every case. The order of fraction of surface covered by butyric acid in decreasing sequence is water, benzene, carbon tetrachloride and cyclohexane.

The vapour-pressure curves show positive deviation for cyclohexane and water systems while the curves for benzene and carbon tetrachloride are almost linear. This shows more affinity between the components in the liquid phase, for the last two systems. So it is suggested that the affinity factor does not support the order of fraction of surface covered by the acid, because this would mean lower adsorption of the acid at the interface for the benzene and carbon tetrachloride systems.

Relative lowering of surface tension of acid + water mixtures is highest for the four systems. This would favour high values of acid adsorption in this system, and hence the maximum fraction of surface covered by the acid in this system is explained. Relative lowering of surface tension in other three systems decreases in the order of benzene, carbon tetrachloride and cyclohexane, the same as the observed order of decreasing preferential adsorption of acid in these systems.

CHAPTER 14.

Thermodynamic correlation with Everett's theory for Adsorption from Solution.

For adsorption at the solid/solution interface a thermodynamic treatment which helps to show how the nature of the solution determines the form of the isotherm in adsorption on to a solid surface from completely miscible liquids has been developed for ideal and regular solutions.[44,45] A more comprehensive treatment for these systems has recently been put forward by Everett.[46,47]

Wright has examined recently, in continuation of his previous work,[39,48] the scope of the thermodynamic theory, and correlations for adsorption from non-ideal binary liquid mixtures containing components of approximately equal sizes.[49] An attempt was made by him to examine how far some systems deviate from perfect surface behaviour.

The reason for examining correlations for perfect surface behaviour in this work is because the interface could be regarded as of Langmuir-type as defined by Everett, (a situation difficult to come by with solid adsorbents), although all the requirements for the properties of the solutions are not satisfied.

An attempt is made here to apply the thermodynamic theory of Everett to two systems with components which have almost the same molecular areas as adsorbed at the interface. Neither of these two systems show strictly perfect surface behaviour.

Propionic acid with a perpendicular orientation at the interface has an area of 20.5 sq.A per molecule. Similarly ethyl alcohol molecule with the same orientation has an area of 22 sq.A. So the molecular areas of both molecules, in the propionic acid + alcohol system, are almost the same. Fig. 61 represents a plot between $\frac{x_1^l x_2^l}{\Gamma_2}$ and x_1^l, the concentration of alcohol in the liquid phase. In this case a linear graph is obtained for x_1^l, between 0.4 and 0.8 but at lower and higher values of x_1^l, the graph deviates, from linearity.

Butyric acid with parallel orientation at the interface has an area of 38 sq.A per molecule and benzene molecule with the same orientation as of the acid has an area 43 sq.A. Fig 62 is a plot between $\frac{x_1^l x_2^l}{\Gamma_2}$ and x_1^l for butyric acid + benzene system. In this case a linear graph is obtained for values of x_1^ℓ up to 0.5 but thereafter the values deviate from linearity. Hence this system too does not show perfect surface behaviour.

Correlations from the thermodynamic theory[46,47] for both the systems thus do not fit with perfect surface behaviour as defined by Everett.

CHAPTER 15.

CONCLUSION.

Although the phenomenon of adsorption has attracted the attention of many scientists in this century, the major part of their contribution has been with the liquid-solid and gas-solid interfaces. However, some workers, already mentioned in chapter 3, have reported results of investigations on adsorption at the liquid-vapour interface, although the contribution of a number of them is limited to the composite isotherms, only(i.e. surface excess isotherms).

Almost all the workers have assumed that the adsorbate at the liquid-vapour interface is confined to the thickness of one molecule. This, as Guggenheim and Adam pointed out[7], is the simplest assumption to be made and hence in the present work the same assumption has been adopted. A treatment put forward by Schofield and Rideal for dilute solutions adds further support to the monolayer hypothesis[15], although some recent work by

Shereshefsky has shown that for some systems, a mean molecular thickness of 2 for the adsorbed phase could be more appropriate.[50]

Benzene. For all the acid systems with benzene, the adsorption of acid increases with increasing acid chain length. It has been suggested that the relative greater lowering of surface tension by acid with increasing chain length is the factor which is dominant over the affinity factor in controlling adsorption. This point is worth noting especially when the behaviour of systems at liquid-vapour and solid-liquid interfaces are to be compared.[27] For the latter interface, several other forces of interaction are often involved in the adsorption process. The orientation of molecules in the above systems has been taken to be the one in which the major axes of the molecules are parallel to the surface,[5, 27, 43] and the results obtained are consistent with this assumption.

It has been noted that in the case of acetic acid + benzene system the composite isotherm, unlike the ones for other two systems, shows a preferential adsorption of benzene at higher concentration of acid in the liquid phase, but this is in agreement with the composite isotherm obtained by Belton for the same system[5].

The individual isotherm for benzene in the acetic acid + benzene system resembles the one put forward by Kipling[51] but the individual isotherm for acetic acid is slightly different from the one given by Kipling for the same system. This difference may be due to differences in molecular areas used in the calculation of individual isotherms.

The individual isotherms for the last two systems reveal that the number of moles of acid per unit area of the surface is quite low at the lower concentrations of acid in the liquid phase but it increases with the increasing acid concentration. Eventually the amount of acid at the interface becomes greater than that of benzene. A unimonolayer of acid is formed only from the pure component.

Everett's general thermodynamic theory for adsorption has been applied to the butyric acid + benzene system and it has been noted that the system does not show a perfect surface behaviour.

Carbon tetrachloride:- The composite isotherms for acetic acid + catbon tetrachloride, propionic acid + carbon tetrachloride and butyric acid + carbon tetrachloride are S-shaped and show that the preferential adsorption of acid increases with the increasing acid chain length. This is suggested to beddue to the increase in the rate of lowering of surface tension by acid with increasing chain length. The most probable orientation of the molecules in these systems is considered to be the one in which the major axes are parallel to the surface, and the results obtained are consistent with this assumption.

The individual isotherms for both the constituents in the three systems show that the amount of acid at the interface increases as the acid concentration in the liquid phase increases and it is high at the higher concentration of acid in the bulk phase. A mixed monolayer over the whole concentration range is noted and a complete monolayer of acid is formed only from the pure component.

Although some of the workers have selected carbon tetrachloride as one of the components of the binary systems they investigated, a general review of the literature shows no work on anyone of these three systems.

Cyclohexane:- The composite isotherms for acetic acid + cyclohexane, propionic acid + cyclohexane and butyric acid + cyclohexane systems show that preferential adsorption of acid decreases with increasing acid chain length. For the first system the isotherm is S-shaped while the other two systems have U-shaped isotherms. The vapour pressure curves reveal decreasing escaping tendency of acid with increasing chain length, from the environment of the solution. They could make a decreasing preferential adsorption of acid with increasing chain length possible. Again, by surface tension factor, relative lowering of surface tension of solution by acid is found to decrease with increasing chain length, an observation which would also explain decreasing adsorption with increasing chain length.

The individual isotherms for both the components in the above three systems show that a uni-monolayer of acid is formed only from the pure component. The orientation of the components has been taken the same as for the benzene systems.

Kipling and Langman[52] have studied the cyclohexane + piperidine system and they found that the isotherm for surface excess was U-shaped. Again Kipling[51] has reported adsorption from mixtures of benzene and cyclohexane at 20°C at the liquid-vapour interface. This isotherm was also U-shaped. Nothing seems to have been recorded in the literature about the behaviour of mono-carboxylic acids in cyclohexane at the solution-vapour interface.

Ethyl alcohol. Acetic acid + ethanol and propionic acid + ethanol systems show regular U-shaped composite isotherms which reveal that it is alcohol which is preferentially adsorbed throughout the whole concentration range of the acid in the liquid phase. It is noted that the adsorption of acid is about the same in both the systems. Preferential adsorption of alcohol seems to arise from the unique ability of ethyl alcohol to decrease the surface tension of acid + alcohol mixtures, throughout the whole concentration range. Both the surface tension and affinity factors are in accord with negative adsorption of the acids.

The overall situation of the interface, as shown by the individual isotherms, is that the amount of alcohol for a greater part of the concentration range is more than that of acid for both systems. A unimonolayer of acid is formed only from pure components. The most probable orientation of the constituents is considered to be the one in which the molecules are perpendicular to the surface.[7, 23]

Butler and Whiteman[21] have discussed the thickness of the adsorbed laywr of ethanol + water system and have found that the observed adsorption is consistent with the hypothesis that only a single layer of molecules at the surface differs incomposition from bulk of the solution. Guggenhiem and Adam[7] also discussed the same system and assumed the layer as unimolecular. Cornford, Kipling and Wright[23] considered the data calculated by Guggenhiem and Adam for the same system and have found that adsorption was confined to approximately one molecular layer, in contrast to earlier suggestions.[21] Kipling[6] discussed the same system and has reported that a complete monolayer of alcohol was formed only from the pure component. In the present work, the same conclusion has been arrived at.

Water: The composite isotherms for the acetic acid + water, propionic acid + water and butyric acid + water systems show that the adsorption of acid increases with increasing acid chain length. This is in accord with decreasing affinity between acid and water, and the greater rate of lowering of surface tension by acid in the above systems, with increasing acid chain length.

The individual isotherms reveal that the number of moles of solvent at the interface is very high at very low concentrations of acid in the liquid phase. This may be due to the relatively small area of the water molecule. The adsorption of acid rises sharply at low concentrations of acid in the liquid phase, but a uni-monolayer of acid is formed only from the pure component. The orientation of the molecules is considered to be the one in which acid molecules are perpendicular to the surface layer, and hydrogen-bonded to water molecules or to other acid molecules. It is suggested that more than one water molecules can be present in the absorbed layer along the length of acid molecule, due to the large differences in molecular areas of the components. Kipling has made similar observations for the butanol + water system.[6]

Many workers have considered ethanol + water system and have concluded that the adsorbed layer was of unimolacular thickness. The water + butyric acid system considered by Fu and Bartell[53] gave a composite isotherm which reached a limiting value, but nothing definite was revealed as to whether there was monolayer adsorption or not. Some workers have considered adsorption from the three systems (acid + water) at the liquid-solid interface, and the composite as well as individual isotherms of the present work show some similarities to some of the isotherms found in literature.

The present investigations have thrown further light on adsorption behaviour at the solution-vapour interface. Too large a percentage of the work in the literature about adsorption behaviour at this interface has been concerned with aqueous systems, and the conclusions generally arrived at, thus tended to be particular rather than general. A complete understanding of the nature of this interface involving a reasonable assessment of thickness of the interface, composition and orientations at the interface, depends on the particular systems involved, on the nature of the solutions, and on the intermolecular interactions possible both in the bulk solution and at the interface.

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