

VERIFIED
INL ... *[Signature]*

[Signature]
19.2.92

COMPUTERISED

CENTRAL CHEMICAL LABORATORY
Th-30 ✓
Date: 18/3/00
L-1

VERIFIED
1901
INL ... *[Signature]*

COMPUTERISED

THERMODYNAMIC PROPERTIES OF ALCOHOLS AND
ALKOXYETHANOLS

COMPUTERISED

A Thesis

Submitted to the University of Bombay
for the Degree of
DOCTOR OF PHILOSOPHY (TECHNOLOGY)

by

Iyer Varadarajan Nagarajan,
B.Sc., B.Sc. (Tech.)

OU: 5367
S41.183
NAG

THE NATIONAL CHEMICAL LABORATORY,

POONA - 8

July 1968



C O N T E N T S

CHAPTER		Page No.
<u>PART – I : SURFACE CHEMICAL STUDIES</u>		
1	Introduction	1
2	Experimental	10
3	Surface thermodynamical properties of methyl, ethyl, propyl and butyl glycols ..	17
4	Properties of aqueous solutions ..	27
5	Determination of the constants in the van Laar equation	37
6	Traube's rule	42
7	Thickness of the adsorbed layer ..	49
8	Individual Isotherms	62
9	Equations of state	74
10	The free – energy of glycol ether adsorption at the air – water interface	86
<u>PART – II : VAPOUR LIQUID EQUILIBRIUM</u>		
1	Introduction	92
2	General methods	98
3	Vapour pressures of pure components ..	102
4	Experimental determination of activity ..	110
	SUMMARY	120
	REFERENCES	123
	SYNOPSIS	128
	ACKNOWLEDGEMENTS ..	131

... and the ...
... the ...
... the ...
... the ...
... the ...
... the ...
... the ...
... the ...

PART - I : SURFACE CHEMICAL STUDIES

...

CHAPTER 1

INTRODUCTION

Monomolecular layers of substances at liquid-air interface form an interesting state of matter. They have more or less two dimensional movement and reduce the surface tension of the liquid phase considerably. It was found that molecules containing a long hydrocarbon chain and a small polar group (-COOH and OH) at one end tended to form closed-packed monolayers on water surface, the molecules being oriented with their polar groups towards water and the hydrocarbon chains above the surface.

Now if a particular monolayer is compact as a result of the adhesive interaction of the polar groups with the water as well as the cohesive (van der Waal's) interaction between the film molecules, an interesting property may arise with regard to the restricted permeability of other molecules such as water vapour through the monolayer. During recent years considerable interest has developed in the practical utilization of this effect towards retarding the evaporation loss of water in lakes and reservoirs.

It is now well established¹ that the insoluble monolayers of the ethylene glycol alkyl ethers such as

normal cetyl and stearyl derivatives, $C_n-OCH_2CH_2OH$ ($n = 16$ to 22) are superior to those of the corresponding alcohols as water evaporation retardants. Many of the nonionic detergents are polyoxyethylene glycol alkyl ethers of the type $C_n-(OCH_2CH_2)_mOH$ where $m > 8$. With a view to elucidate the behaviour of monolayers formed by such compounds, a study of the surface chemical properties of the lower members of the homologous series, such as the methyl, ethyl, propyl and butyl glycol in water solution is considered desirable so that they may serve as simpler models helpful to a better understanding of more complex molecular systems.

When a second component is added to a pure solvent, it is usually found that the surface layer has a different composition from that of the bulk of the mixture. The extent of adsorption on the surface or the 'surface excess' greatly influences the nature of the liquid-vapour interface and this aspect has been studied in terms of experimental data on surface tension by many investigators⁴. We are thus led to a very important topic, namely, the thermodynamic treatment of the variation of surface tension with composition. The treatment is due to Gibbs², but has been amplified by Guggenheim and Adam³.

As has been discussed in later chapters, from surface tension data and the Gibbs equation, many surface thermodynamic and structural properties may be derived. If the surface tension of a liquid is lowered by the addition of a solute, it follows from the Gibbs equation that the solute is adsorbed at the interface. This may eventually amount to enough to correspond to a monomolecular layer of the solute on the surface with a certain thickness and orientation.

Surface chemical properties of aqueous solution of the alkyl glycol ether type of compounds have been published recently by Shinoda, Yamana^Kba, Kinoshita⁵. The surface tension (γ) - $\log c$ (concentration) curves showed inflections corresponding to the critical micelle concentration (c.m.c) values (or the maximum concentration of molecular dispersion).

Shinoda and collaborators estimated the area per molecule in the monolayer state under the assumption that $\partial \ln a / \partial \ln c = 1$, where a is the activity of the solute. The values were 30 \AA^2 for octyl alcohol and 32 \AA^2 for octyl glycol water.

The n-butyl, n-octyl, n-dodecyl and n-hexadecyl monoethers of hexaoxyethylene glycol were prepared by Corkill, Goodman, and Ottewill⁶. The c.m.c.'s were determined at 25° by measuring the γ against $\log c$ curves.

From a plot of log (c.m.c) against the number of carbon atoms in the hydrophobic chain for the homologous series, the standard free-energy per CH₂ group of a single molecule on micellization was found to be 1.10 kT.

Schick⁷ worked on polyoxyethylene n-dodecanol and n-octadecanol, where the number of oxyethylene groups varied from 1 to 100 and concluded that the hydrophilic ethylene oxide chains formed coils in the aqueous phase and hydrophobic groups oriented above the interface. He ruled out a horizontal orientation of the ethylene oxide chains in the adsorbed film.

Lovell and Hibbert⁸ measured the effect of concentration of various polyglycols on the surface tension of their aqueous solution

All the four glycols with number (P) of -CH₂-O-CH₂- groups equal to 18, 42, 90 and 186 showed a constant adsorption over the entire concentration range, the slope dγ/dlogc, being constant. This indicated the formation of a saturated surface layer and as all the concentrations were very small, the area per molecule was calculated directly from the slopes of the log curves. For comparison, the areas calculated ^{by Kraem} on the basis of horizontally oriented zigzag chains are indicated in table A.

Table - A

Molecular areas of higher glycols

P	A (found) \AA^2	A zigzag (calculated)
18	216 \pm 30	223
42	287 \pm 10	512
90	235 \pm 10	1088
186	79	2235

The authors concluded that the long chains tended to assume a vertical orientation as the chain length was increased and the ether group did not anchor the chains parallel to the substratum.

Another interesting study of the adsorption of polyoxyethylene glycols on the surface of aqueous solutions is by Couper and Eley⁹. The surface tension, viscosity freezing point depression and density as a subsidiary to viscosity were measured. The surface tension measurements made at room temperature varied linearly with log c.

Applying the Gibbs equation, it was deduced that the surface excess was constant over the range of concentrations measured. Its magnitude, for four fractions of different

molecular weight, corresponds to the formation of a complete monolayer with the major axes of the molecules parallel to the surface. The area per molecule calculated by $\Gamma = 1/NA$, where Γ is the surface excess in moles per sq.cm., N the Avogadro's number and A is the area/molecule, is shown below.

<u>Polyoxyethylene glycol fraction</u>	<u>A in \AA^2/molecule</u>
1000	440
1540	530
4000	1030
6000	2390

A comparison was also made between the area per adsorbed polymer molecule in the surface and the average molecular weight as given by intrinsic viscosity and freezing point data. The absolute values of the area per molecule and their change with molecular weight as noted in table B below, strongly support the view that the adsorbed molecules lie flat in the water surface in disagreement with the earlier work of Lovell and Hibbert, who claimed a tendency for the higher polyglycols to orient vertical to the surface as in the case of fatty acids.

Table - B

Relative values of molecular size

Fraction	Viscosity	Freezing point		Area
		Water	Nitrobenzene	
1000	1.00	1.00	1.00	1.00
1540	1.18	1.23	1.27	1.204
4000	2.04	1.76	2.08	2.34
6000	2.09	2.78	2.65	5.41

STUDY ON HOMOLOGUS SERIES OF COMPOUNDS HAVING DIFFERENT
END GROUPS

The regularities which are often observed in the physical properties in the bulk of a homologous series also extend at the interfaces. The first important generalisation was made by Traube¹⁰ on the surface tensions of aqueous solutions of organic solutes. He found that the surface activity increased strongly and regularly as any series was ascended.

Szyskowski¹¹ measured surface tensions of aqueous solutions of propionic, butyric, valeric and caproic acids and found that results could be accurately expressed by an empirical equation.

$$\frac{\gamma}{\gamma_0} = 1 - B \log_{10} \left(\frac{C}{A} + 1 \right)$$

where γ_0 is the surface tension of water, A and B are constants, and C is the concentration. B was found to be the same for all fatty acids studied and A decreased rapidly as the length of hydrocarbon chain increased. No reason was given for constancy of B and change in A.

Addison¹² studied the surface tension of aqueous solutions of alcohols upto octyl alcohol at one temperature (20°). The static tensions at high concentration were used to evaluate the Szyskowski's constants and the work of adsorption (free energy) was deduced from the static tensions at great dilution.

The temperature dependance study of Addison and Hutchinson¹³ was limited to solutions of decyl alcohol only.

Alexander, Anderson and Posner¹⁴ undertook a systematic study of the homologous series of normal aliphatic alcohols. From the temperature dependence of surface tension the quantities ΔH° , ΔS° and ΔG° for the adsorption process were calculated. These results were correlated with corresponding solution thermodynamical data. The molecular configuration in the surface was tentatively deduced. The surface phase more closely resembled the bulk solution than

the vapour. The negative entropy of adsorption from the vapour phase was very large and it was suggested that additional factors responsible for the high values were changes in internal degrees of freedom of the hydrocarbon portion of the molecule and 'cluster' formation in the immediate neighbourhood of the solute molecule.

For aqueous solutions King and Wampler¹⁵ found that dicarboxylic acids were less strongly adsorbed than the monocarboxylic acids and attributed this to the greater attraction of water for two carboxylic groups than one. Correspondingly the esters were more strongly adsorbed than the acids, because the ester group was less polar than the carboxyl group.

No systematic surface chemical study has been done on a homologous series of ether-alcohol type of compounds, which are interesting from the theoretical view point and also important industrially. As indicated before, we report the results of our study of the lower members of the series, namely those of methyl, ethyl, propyl and butyl-glycols in the pure as well as in the aqueous solution state.

CHAPTER 2

EXPERIMENTAL

MATERIALS

The methyl, ethyl and butyl glycols used here, $R-OCH_2CH_2OH$ where $R = CH_3, C_2H_5$ and C_4H_9 have been carefully purified from commercial materials by fractionation at atmospheric pressure, using a spinning band type fractionation column with high reflux ratio. The commercially unavailable propyl glycol has been synthesised by reaction between Na-propyl alcoholate and ethylene chlorohydrin¹⁶. All attempts made to synthesise the above compound by Williamson's ether synthesis according to Palomaa¹⁷ were unsuccessful as the diether formed in small quantities could not be separated from the required monoether by fractionation.

The purity of all these compounds were checked by the Gas liquid chromatographic technique. All these ethers gave a single peak.

Water was redistilled from alkaline permanganate solution using an all glass pyrex still. The solutions of known composition were prepared by weighing accurately appropriate amounts of purified glycol ethers and water into dried, stoppered, tared, 150 ml. conical flasks.

Solutions having film pressure π less than 3 dynes/cm were prepared by successive dilution.

The data on refractive index, density and surface tension for the purified glycol ethers gave excellent checks with those previously reported in the literature.

METHODS

(a) Surface tension :

The measurement of the surface tension of pure liquids and solutions can be made by a variety of techniques. Adam¹⁸ and Bikerman¹⁹ listed some twelve methods many of which have been modified later.

The capillary rise method is generally considered to be the most accurate of all methods. However, for practical reasons a zero contact angle is required and fairly large volumes of solution are needed. One experimental difficulty is the need to obtain a section of capillary tubing sufficiently uniform in radius over the operating range.

The maximum bubble pressure method does not depend on contact angle and measurements can be made rapidly. The method is a quasi-dynamic one in that freshly formed liquid-air interfaces are involved.

In the drop weight method an important precaution to take is to use a tip that has been ground smooth at the end

and which is free from any nicks. For volatile liquids, some sort of closed system should be employed so as to eliminate evaporation losses. The drops should be formed slowly.

The Wilhelmy slide and the ring methods are capable of good precision and the latter becomes essentially an absolute method if the correction factors of Harkins and Jordan²⁰ are used. The ring must be flamed before use, be kept horizontal and care be taken to avoid ripples on the liquid surface as the critical point of detachment is approached.

The sessile drop and pendant drop are static methods based on the shape of static drops or bubbles. The vibrating jet method is a dynamic method of measuring surface tension. Harkins advocated the drop weight method as the best for measurement of surface and interfacial tensions of solutions if long time effects are not involved, the sessile bubble method if long time effects are involved and the ring method for surface tension measurements in either case. Hommelen²¹ successfully measured the surface tension of aqueous solutions of n-hexyl, n-heptyl etc., alcohols using the ring method, taking care to see that the liquid surface was in equilibrium with the saturated vapour.

We have employed the ring method. A chainomatic balance especially modified for surface tension measurements was used in this study. The balance was used in conjunction with a platform which could be raised and lowered smoothly and slowly in a water bath, thus enabling the test solution to be thermostated. The balance was sensitive to 0.05 mg. and the rider and weights were calibrated with certified weights before use. To obtain good results it was necessary to insulate the balance from vibration. The ring was levelled by bringing a dish of mercury close to it and sighting between the ring and the mercury surface. A very small deviation from the level could be determined in this fashion.

The liquid was held in a conical flask and fitted with a cover of plate glass. The cover was slotted to permit the wires supporting the ring to pass through. This arrangement worked satisfactorily in minimizing evaporation of even the most volatile liquids of this study.

The procedure was as follows : A clean conical flask containing the experimental liquid was placed on the platform, the cover was put in place and the whole system allowed to come to thermal equilibrium in a thermostat to ensure that the space above the liquid became saturated with vapour. The liquid was then raised till it touched the ring. Weights were added and platform simultaneously

lowered to keep the balance pointer at zero. When the final addition of 0.1 mg. made the pointer swing irreversibly to the left the weight was recorded as the maximum pull on the ring. Successive measurements made in this fashion were invariably within ± 0.1 mg. of each other.

The performance of the chainomatic balance and the ring were checked against distilled water at different temperatures and several reagent grade chemicals at 20°C. Some of the results are noted in Table I.

It is seen that our results are in good agreement with the literature data.

(b) Density :

A precision balance (0.01 mg accuracy) was adapted to density measurements by attaching to the balance arm a fine platinum wire at the end of which is fastened a cylinder of pyrex glass of volume 5.260 ml/25°C. The wire passed through a hole in the platform of the balance so that the pyrex glass sinker could be conveniently immersed in a column of thermostated liquid, placed below the balance case.

The combined sinker and wire were weighed first in air, then in the liquid. The surface of the liquid was brought to the same mark on the platinum wire each time so that the wire always contributed the same (small) amount

to the total volume of the immersed plummet. The reproducibility of measurements of 'd' was better than ± 0.0001 gms per ml. The uncertainty arising from the surface tension effect between the liquid surface and the wire was calculated and densities corrected. All weighings at 25° were reduced to values in vacuo.

The accuracy of the method was ascertained by making observations on a series of water-ethyl alcohol solutions for which reliable values of density are available in the literature. A few measurements of density were also checked by using a Lipkin type bicapillary pycnometer which had been calibrated using boiled distilled water. All these data compared well with each other.

TABLE I

Calibration of ring balance

Substance	Wt. to pull out ring M mgms.	Mg/4πR=P	Density of liquid d gm/ml.	M/d = V	R ³ /V mls.	Harkins' correction factor f	Surface tension Pf=Y dynes/cm	Lit. value dynes/cm.
Distilled water	15° 0.6237	74.36	0.9991	0.6243	0.448	0.988	73.47	73.49
	20° 0.6181	73.69	0.9982	0.6192	0.451	0.988	72.81	72.75
	25° 0.6140	73.20	0.9971	0.6158	0.454	0.988	72.33	71.97
	30° 0.6070	72.37	0.9957	0.6096	0.459	0.985	71.28	71.18
	35° 0.5979	71.28	0.9941	0.6015	0.465	0.984	70.14	70.38
Nitro- benzene	20° 0.3949	47.12	1.2032	0.3282	0.852	0.926	43.64	43.35
Benzene	20° 0.2652	31.65	0.8790	0.3017	0.927	0.919	29.08	28.88
Ethyl alcohol	20° 0.2082	24.85	0.7895	0.2637	1.06	0.909	22.58	22.32

Diameter of ring 1.3077 cms ; Radius of ring R = 0.6539 cms ; Radius of wire r = 0.0153 cms.,
 R³ of ring = 0.2795 ; R/r = 42.88 ; g = acceleration due to gravity.

CHAPTER 3

SURFACE THERMODYNAMICAL PROPERTIES OF METHYL, ETHYL,
PROPYL AND BUTYL GLYCOLS

INTRODUCTION

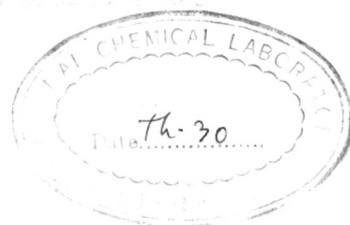
The liquid surface refers to a region of indefinite thickness between liquid and gas phases. Thermodynamics which is very successful in defining the properties of three dimensional systems, can also be applied to the liquid surface region which can be regarded as a two dimensional independent phase. Equations which relate the properties in the liquid surface region are presented below. A brief description of how these equations are applied will be helpful in evaluating the significance of thermodynamic data in determining the properties of this region.

Lord Kelvin was the first to apply the following two dimensional form of the equation of Clapeyron to the liquid surface region,

$$- \frac{d\gamma}{dT} = L^s/T \Delta A \quad \dots (1)$$

in which L^s is the latent heat of surface formation and ΔA is the increase in the total surface area. Since the

04:591.183
NAG



surface properties are intensive variables, ΔA is equal to unity and the equation reduces to the more simple form,

$$- \frac{d\gamma}{dT} = \frac{L^s}{T} = \Delta S^s \quad (2)$$

Since a molecule which is in the interior of a liquid must move into the surface against the attraction of the surrounding molecules, molecular kinetic energy is utilized and transformed into potential energy of the surface. The heat that is used in the formation of the surface is L^s , which therefore represents the quantity of thermal energy that must be added to the liquid system while the surface is undergoing isothermal expansion by one cm^2 . The quantity L^s/T is the entropy change attending the formation of unit area of liquid surface and is designated as the entropy of surface formation - ΔS^s . The equation (2) may be rearranged as follows

$$- T \left(\frac{d\gamma}{dT} \right) = L^s \quad \dots (3)$$

The well known free energy equation $F = H - TS$ enables the calculation of the total surface energy, the enthalpy of surface formation. The two dimensional form of this equation when applied to liquid surface, is written as follows

$$H^s = F^s - TS^s \quad \dots (4)$$

Therefore, for conditions of constant pressure and

volume,

$$H^S = \gamma - T \left(-\frac{\gamma}{T} \right)_{p,v} = \gamma - L^S \quad \dots (5)$$

It is evident, therefore, that the total surface energy involves both the free surface energy and the latent heat of surface formation.

RESULTS

In what follows we have presented some surface thermodynamical properties derived from surface tension data. Table 1, 2, 3 and 4 give data on the properties of glycol ethers. They are in good agreement with those previously reported^{22,23,24,25}. The surface tensions and latent heats of surface formation over a range of temperature show that both these changes linearly with temperature. The former decreases while the latter increases at almost exactly the same rate. The enthalpy of surface formation of glycol ethers, like most pure liquids, is practically independent of temperature.

The linear variations of surface tensions and latent heats of surface formation with temperature may be represented by the following equations

$$\gamma = a - bT \quad \dots (6)$$

and

$$L^S = c + dT \quad \dots (7)$$

The specific constants, a, b, c and d for the series are presented in Table 4. According to equation (5), the enthalpy of surface formation at any temperature can be calculated by combining equations (6) and (7) to give

$$\Delta H^S = a + c + t (d - b) \quad \dots (8)$$

Considering the entropy as a measure of disorder, the formation of the liquid surface region is attended by a decrease in entropy. The entropy of the liquid surface region may be regarded a measure of molecular orientation. The negative temperature coefficients of surface tension are the entropies of surface formation. This decreases with increasing molecular weight. This seems to indicate that the degree of order in the liquid surface region increases with increase in chain length. Similar results were obtained by Adam¹⁸ for homologous series of hydrocarbons, acids, amines and triglycerides.

EÖTVÖS EQUATION

If M is the molecular weight and v the specific volume of the liquid, Eötvös equation is

$$(Mv)^{2/3} \gamma = k (T_c - T - T_x)$$

The correction term (T_x) was introduced by Ramsay and Shields²⁶. $(Mv)^{2/3}$ is termed 'molar surface area'.

Eötvös believed 'k' in the above equation to be a universal constant (2.12 erg/deg). Hence it should be possible to calculate M for any liquid for which critical temperature, surface tension and specific volume have been evaluated, by use of the equation

$$M^{2/3} = 2.12 (T_c - T - 6) / (\gamma v)^{2/3}$$

But it is now well known that many substances give low or high molecular weights (as compared with their chemical formula weight) when calculated according to the above equation. The Eötvös constants for alkyl glycols are indicated in Table 4. The critical temperatures required for the calculation were obtained by the group contribution method of Hougen, Watson and Ragatz²⁷. For the alcohols 'k' varied between 0.95 to 1.5, whereas the value for alkyl glycols it is between 1.4 to 1.6.

The parachor introduced by Sugden belongs, in addition to the molar refraction, to the most known quantities, which are known as additive. This means that they can be with a certain accuracy calculated as the sum of increments for the individual elements of the given structure. Recently Exner²⁸ evaluated the significance of the parachor as an additive quantity by comparing with molar volumes. The accuracy of the additive relation was

shown to be not high and so the parachor as an additive quantity was rejected.

Parachor, however, has been used for calculating the van Laar constants for mixtures of members of a homologous series (n-alcohols-water), if these constants are known for at least two systems of the series under consideration²⁹. A semi-empirical method was also proposed for the determination of the above constants, from the properties of pure constituents parachor being one of the properties³⁰.

The parachor values of alkyl glycols calculated from surface tension and density measurements are indicated in Table 4 and also used for calculating the van Laar constants in Chapter 5.

TABLE 1

Properties of pure compounds

Surface tension - dynes/cm

	5°C	15°C	25°C	35°C	45°C	55°C	65°C	Earlier data
Methyl glycol	32.26	31.85	30.66	29.70	28.77	27.96	-	31.82 at 15°C (22)
Ethyl glycol	29.84	29.16	28.28	27.36	26.23	25.14	24.48	28.46 at 25°C (22)
n-propyl glycol	28.96	28.44	27.51	26.66	-	-	-	-
n-butyl glycol	28.85	28.39	27.43	26.71	25.63	24.99	24.14	27.80 at 20°C (23)

TABLE 2

Properties of pure compounds

Density - gms/ml.

	15°	20°	25°	30°	35°	Earlier data
Methyl glycol	0.9688	0.9646	0.9598	0.9561	0.9517	0.9602 at 25° (24)
Ethyl glycol	0.9340	0.9293	0.9250	0.9206	0.9161	0.9252 at 25° (24)
n-propyl glycol	0.9149	-	0.9062	-	0.8979	0.9112 at 20° (25)
n-butyl glycol	0.9044	0.9007	0.8960	0.8924	0.8883	0.8966 at 25° (24)

TABLE 3

Properties of pure compounds
Refractive index - Visible light

	At 20°C	Earlier data
Methyl glycol	1.4015	1.4021 (24)
Ethyl glycol	1.4073	1.4077 (24)
n-propyl glycol	1.4130	1.4133 (25)
n-butyl glycol	1.4183	1.4193 (24)

TABLE 4

Specific constants for the temperature relations of the surface tension (a, b)
and latent heats of surface formation (c, d)

Compound	a	Entropy of surface formation b ergs/cm ²	c	d	Enthalpy of surface formation ΔH^S ergs/cm ²	Parachor $M^{1/4} d^{-1}$	Eötös constant k ergs/deg.
Methyl glycol	33.1	0.100	27.3	0.100	60.60	186.6	1.60
Ethyl glycol	30.7	0.095	26.0	0.096	56.48	224.7	1.64
n-propyl glycol	29.6	0.085	23.2	0.086	52.78	262.7	1.70
n-butyl glycol	29.6	0.085	23.2	0.086	52.78	302.3	1.40

CHAPTER 4

PROPERTIES OF AQUEOUS SOLUTIONS

To provide a simple but precise method for the analysis of glycol-ether-water solutions, the densities of the above solutions were determined at different temperatures, over the entire composition range and refractive index data were also obtained at one temperature (30°C). Although values of these properties have been reported in the literature for the methyl and ethyl derivatives at 25°C ²⁴ and for the butyl derivative at other temperatures also³¹, no data have been given for the propyl derivative and for methyl and ethyl at different temperatures.

The density values of the solutions have been utilised in the calculation of the Harkins and Jordan²⁰ correction factors to be applied for the measured values of surface tension. The refractive index and density values were also utilized in knowing the composition of the two phases during vapour-liquid equilibrium measurements.

Our results are listed in Tables 5, 6, 7 and 8.

Where comparable, the values are found to be in agreement with those of Yu Chu and Thompson²⁴ and Onken³¹. The curves

for the first three members of the series show maxima and in the vicinity of the maximum in each of the three density curves (not shown) the change in density with composition is relatively slight. Hence, analysis of vapour and liquid composition by density is not satisfactory in this region.

The surface tension values for aqueous solutions at different temperatures are shown in Tables 9, 10, 11 and 12.

TABLE 5

Absolute density and refractive index of alkyl glycol ether solutions

Weight percent	G/ml at 15°	20°	25°	30°	35°	Refractive index 30°
Water	0.99913	0.99823	0.99707	0.99568	0.99406	1.3332
20.33	1.0056	1.0040	1.0026	1.0005	0.9979	1.3511
40.09	1.0130	1.0103	1.0067	1.0035	1.0002	1.3681
49.56	1.0135	1.0100	1.0063	1.0026	0.9989	1.3759
60.00	1.0104	1.0066	1.0024	0.9985	0.9943	1.3826
68.80	1.0050	1.0011	0.9969	0.9929	0.9886	1.3881
80.78	0.9936	0.9595	0.9853	0.9813	0.9769	1.3936
89.96	0.9831	0.9789	0.9744	0.9701	0.9658	1.3968
Methyl glycol	0.9688	0.9646	0.9600	0.9561	0.9517	1.3995

TABLE 6

Absolute density and refractive index of ethyl glycol solutions

Weight percent	Density in g./ml. at				Refractive index 30°
	15°	20°	25°	30°	
Water	0.99913	0.99823	0.99707	0.99568	1.3332
19.17	1.0031	1.0002	0.9982	0.9959	1.3529
29.32	1.0040	1.0011	0.9985	0.9955	1.3629
38.26	1.0023	0.9997	0.9965	0.9929	1.3711
58.16	0.9919	0.9877	0.9838	0.9796	1.3870
68.49	0.9815	0.9771	0.9730	0.9688	1.3932
78.29	0.9691	0.9648	0.9606	0.9563	1.3981
89.55	0.9521	0.9479	0.9436	0.9393	1.4021
Ethyl glycol	0.9340	0.9293	0.9250	0.9206	1.4050

TABLE 7

Absolute density and refractive index of n-propyl glycol solutions

Weight percent	Density in g./ml. at			Refractive index 30°
	15°	25°	35°	
Water	0.99913	0.99707	0.99406	1.3332
20.39	0.9981	0.9932	0.9872	1.3503
30.35	0.9944	0.9883	0.9815	1.3652
40.17	0.9877	0.9807	0.9735	1.3724
49.95	0.9785	0.9540	0.9455	1.3822
66.86	0.9615	0.9415	0.9334	1.3945
77.17	0.9472	0.9367	0.9287	1.4011
80.41	0.9448	-	-	1.4031
89.83	0.9322	0.9240	0.9147	1.4083
n-propyl glycol	0.9149	0.9062	0.8979	1.4105

TABLE 8

Absolute density and refractive index of n-butyl glycol solutions

Weight percent	Density in g./ml. at			Refractive index 30°		
	15°	20°	25°		30°	35°
Water	0.99913	0.99823	0.99707	0.99568	0.99406	1.3333
18.57	0.9922	0.9899	0.9872	0.9848	0.9821	1.3536
28.76	0.9838	0.9812	0.9783	0.9756	0.9724	1.3632
37.47	0.9765	0.9734	0.9703	0.9670	0.9639	1.3712
53.64	0.9592	0.9558	0.9519	0.9483	0.9448	1.3881
68.19	0.9476	0.9438	0.9401	0.9362	0.9323	1.3972
79.17	0.9355	0.9315	0.9273	0.9233	0.9193	1.4052
89.18	0.9222	0.9180	0.9141	0.9094	0.9053	1.4119
n-butyl glycol	0.9044	0.9007	0.8960	0.8924	0.8883	1.4160

Table 9

Surface tension of aqueous solutions of
methyl glycol

Concentration g.mol/L	Surface tension, dynes/cm. at		
	15°	25°	35°
0.0262	72.50	71.30	70.10
0.0524	72.35	70.60	69.05
0.1048	70.65	69.20	67.95
0.1200	70.32	68.77	66.01
0.2285	68.66	67.12	65.10
0.3464	67.18	65.24	63.17
0.5506	64.51	62.95	61.48
0.9271	61.53	60.02	58.55
1.5380	58.13	56.38	54.65
2.6789	53.63	51.82	50.38
5.3041	45.40	44.09	43.02
6.5539	42.58	41.46	40.36
7.9046	39.68	38.59	37.73
9.0235	37.83	36.58	35.86
10.4625	35.46	34.44	33.50
11.1944	33.74	32.64	31.82
Methyl glycol	31.85	30.66	29.70

TABLE 10

Surface tension of aqueous solutions of
ethyl glycol

Concentration g.mol/l	Surface tension, dynes/cm. at		
	15°	25°	35°
0.0102	72.40	71.10	69.80
0.0203	72.00	70.45	69.20
0.0406	70.40	69.35	67.95
0.0425	70.00	68.77	65.79
0.0978	68.01	66.41	63.60
0.1880	65.08	63.28	61.34
0.4870	60.02	57.96	56.10
1.0690	53.94	51.86	49.45
2.1233	47.00	45.01	42.90
3.2485	41.80	40.18	38.70
4.2304	38.66	37.32	36.09
6.3487	34.56	33.68	32.80
7.3948	33.15	32.28	31.39
8.3450	31.54	30.77	30.34
9.3760	30.55	29.61	28.82
Ethyl glycol	29.16	28.28	27.36

TABLE 11
 Surface tension of aqueous solutions of
 n-propyl glycol

Concentration g.mol/l	Surface tension, dynes/cm. at		
	15°	25°	35°
0.0039	72.40	71.10	69.65
0.0078	71.40	70.35	68.88
0.0156	70.45	68.65	67.55
0.0161	69.70	68.41	65.32
0.0235	68.83	67.35	64.65
0.0432	66.14	64.26	61.56
0.0704	62.91	61.59	58.61
0.2141	55.53	53.90	52.32
0.4186	50.18	47.86	46.63
0.8814	42.77	40.51	38.99
1.3183	38.76	36.56	35.14
1.7590	35.62	34.24	32.32
2.8661	31.85	31.06	30.07
5.2390	30.33	29.71	28.92
6.0310 glycol	29.97	29.25	28.56
6.7740	29.68	28.93	28.15
7.5478	29.34	28.56	27.76
8.0682	29.03	28.31	27.31
n-propyl glycol	28.44	27.51	26.66

TABLE 12

Surface tension of aqueous solutions of
n-butyl glycol

Concentration g.mol/l	Surface tension, dynes/cm. at		
	15°	25°	35°
0.0012	72.25	71.10	69.75
0.0025	71.90	70.40	69.13
0.0049	70.25	68.90	67.60
0.0093	67.77	66.42	64.75
0.0098	67.95	66.50	65.70
0.0246	63.08	61.20	-
0.0442	59.14	57.16	55.60
0.0860	53.36	51.18	49.57
0.2137	44.91	42.68	40.70
0.3959	38.57	36.50	34.47
0.7664	31.37	29.56	27.99
1.5516	28.28	27.66	26.97
n-butyl glycol	28.39	27.43	26.71

CHAPTER 5

DETERMINATION OF THE CONSTANTS IN THE VAN LAAR
EQUATION

For calculating the surface excess using the accurate form of Gibbs adsorption equation, activity data are also required. The practice has usually been to calculate activity coefficient from experimental vapour-liquid equilibrium data at the same temperature as surface tension, but this is time consuming and sometimes too difficult to be practicable.

There is a definite relationship between the activity coefficient values for the two components in a binary system. This is expressed by the Gibbs-Duhem equation

$$x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} = x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_2} \right)_{T,P}$$

where x_1 and x_2 are mole fractions of the two components and γ_1 and γ_2 are the activity coefficients. The most useful mathematical solutions of this differential equation are the equations derived by van Laar³², which are given below in a slightly rearranged form³³

$$\log \gamma_1 = \frac{A}{\left(1 + \frac{Ax_1}{Bx_2}\right)^2}$$

$$\log \gamma_2 = \frac{B}{\left(1 + \frac{Bx_2}{Ax_1}\right)^2}$$

In this form the constants A and B have the property of being equal to the terminal values of $\log \gamma$ in the $\log \gamma_1$ and $\log \gamma_2$ vs concentration curves respectively.

Thus at $x_1 = 0$, $\log \gamma_1 = A$ and at $x_1 = 1$ when $x_2 = 0$, $\log \gamma_2 = B$. As this involves extrapolation of $\log \gamma$ values to infinite dilutions which is of very uncertain accuracy, the ideal situation would be one in which these activity coefficients could be predicted from the properties of pure components. For polar substances Hala, Pick, Fried and Vilim have suggested a method²⁹ for the calculation of the van Laar constants for a whole group of substances from the parachors of these constituents and from the known values of the constants for standard binary systems.

It is based on the relation

$$A_{1,3}^{0.5} - A_{1,2}^{0.5} = K \frac{N_2 - N_3}{N_2 N_3} \quad \dots (1)$$

and

$$B_{1,3}^{0.5} - B_{1,2}^{0.5} = K' \frac{N_2 - N_3}{N_1} \quad \dots (2)$$

where $A_{1,3}$ and $A_{1,2}$, $B_{1,3}$ and $B_{1,2}$ are the constants of van Laar equation of the system 1,2 and 1,3 and the constants K

and K' are to be determined for the group of 2 component systems. The quantities N_1, N_2, N_3 are related to the parachor (P) by the equation

$$N_1 = (0.366 [P]_1 + 11.0)^{0.625}$$

The experimental van Laar constants of the systems methyl glycol-water and ethyl glycol-water are known^{34, 35}. Accordingly, the constants of n-propyl glycol and n-butyl glycol-water systems have been evaluated by us as shown below.

Parachor values of components		Values of constant N_1
Water	54.2	8.61
Methyl glycol	186.6	15.63
Ethyl glycol	224.7	17.30
Propyl glycol	262.7	18.88
Butyl glycol	302.3	20.45

For the system methyl glycol-water, the value of A at approximately 50°C is 0.054 and of B is 0.264. For the system ethyl glycol-water, at approximately 55°C A is 0.26 and B is 0.67.

The constants K and K' for the binary systems of alkyl glycol-water are calculated using formula (1) and (2) and with the known constants A and B noted above.

$$K = \frac{(0.67^{0.5} - 0.264^{0.5}) \times 15.63 \times 17.30}{(17.30 - 15.63) \times 8.61}$$

$$= 5.73$$

$$K' = \frac{(0.26^{0.5} - 0.054^{0.5}) \times 8.61}{(17.3 - 15.52)}$$

$$= 1.431$$

The van Laar constants of propyl glycol/water and butyl glycol/water systems were calculated by substituting these values of K and K' and the corresponding parachor values in the equation (1) and (2). These are indicated in the Table C.

Table - C

System	Van Laar's constants	
	A	B
Methyl glycol	0.054	0.264
Ethyl glycol	0.26	0.67
n-propyl glycol	0.5968	1.118
n-butyl glycol	1.0681	1.743

The B value (1.743) of n-butyl glycol-water system shows good

agreement with 1.74 calculated from solubility data of Cox and Cretcher³⁶ and 1.85 calculated by Wilson and Deal³⁷ on the basis of group contributions.

It may be relevant to mention here that there are other equations such as Margules, Scatchard and Hamer, which express the activity coefficients of both components of a binary mixture. The clue as to which equation to use follows from values of molar volume. Since the binary systems under consideration include water and the molar volumes are different, the van Laar equation is more suitable. Although this procedure is reliable some precautions are necessary in its use, where the vapours depart appreciably from the ideal behaviour. When there is a wide difference between the end values (A and B), the agreement between the experimental activity coefficients and those calculated by van Laar equations may not be satisfactory. The effect of temperature on activity coefficients also needs to be considered. The change of A and B with temperature may be related to L (partial molal enthalpy) at $x_1 = 0$ and $x_1 = 1$, respectively. For aqueous solutions this change is not so simple in as much as the value of L frequently reverses its sign in the ordinary temperature range. However, in the absence of experimental data for all the systems the above procedure can be adopted as an approximation.

CHAPTER 6

TRAUBE'S RULE

INTRODUCTION

Many organic substances such as alcohols, aldehydes, fatty acids, esters and amines are surface active in aqueous solutions. The change of the surface tension of a liquid with increasing concentration of the solute is clearly illustrated by the γ -C curves. For example, pure formic, acetic, propionic and butyric acids have very similar surface tensions. But if dissolved in water, they lower its surface tension in proportion to the length of the chain of the respective fatty acid. This is the essence of Traube's rule, which states that the surface activity of fatty acids increases regularly with ascent of the homologous series. In order to achieve the same lowering of γ of water, an amount which is approximately one third as much of the next higher acid in the series is necessary. For instance, 1.38 moles/l of formic acid lower the surface tension of water by 14%. The same effect can be produced by a 10000 times smaller amount of n-nonanoic acid. The behaviour of alcohols, esters and amines arranged according to their chain length is similar.

We are interested to investigate the surface active behaviour of a series of alkyl glycols in water and the results in terms of the surface tension data, are reported in the following.

RESULTS AND DISCUSSION

Fig.1 shows film pressure (π) as given by $\gamma_{\text{solvent}} - \gamma_{\text{solution}}$ vs. concentration (c) curves for glycol ethers at 25°C. $d\pi/dc$ is initially constant (0-3 dynes/cm) followed by a continuous decrease. The Traube rule, $\pi = ac$ holds in this region for all the members. As expected $\alpha_n/\alpha_{n-1} \approx 3$ (where n is the number of carbon atoms in the molecules),

Table - D

<u>n/n-1</u>	<u>α_n/α_{n-1}</u> <u>0-3 dynes/cm.</u>
2/1	75/26.1 = 2.88
3/2	214/75 = 2.85
4/3	623/214 = 2.92
	Mean = 2.88

Langmuir³⁸ gave an instructive interpretation to this rule. Accordingly, the work W , to transfer one mole

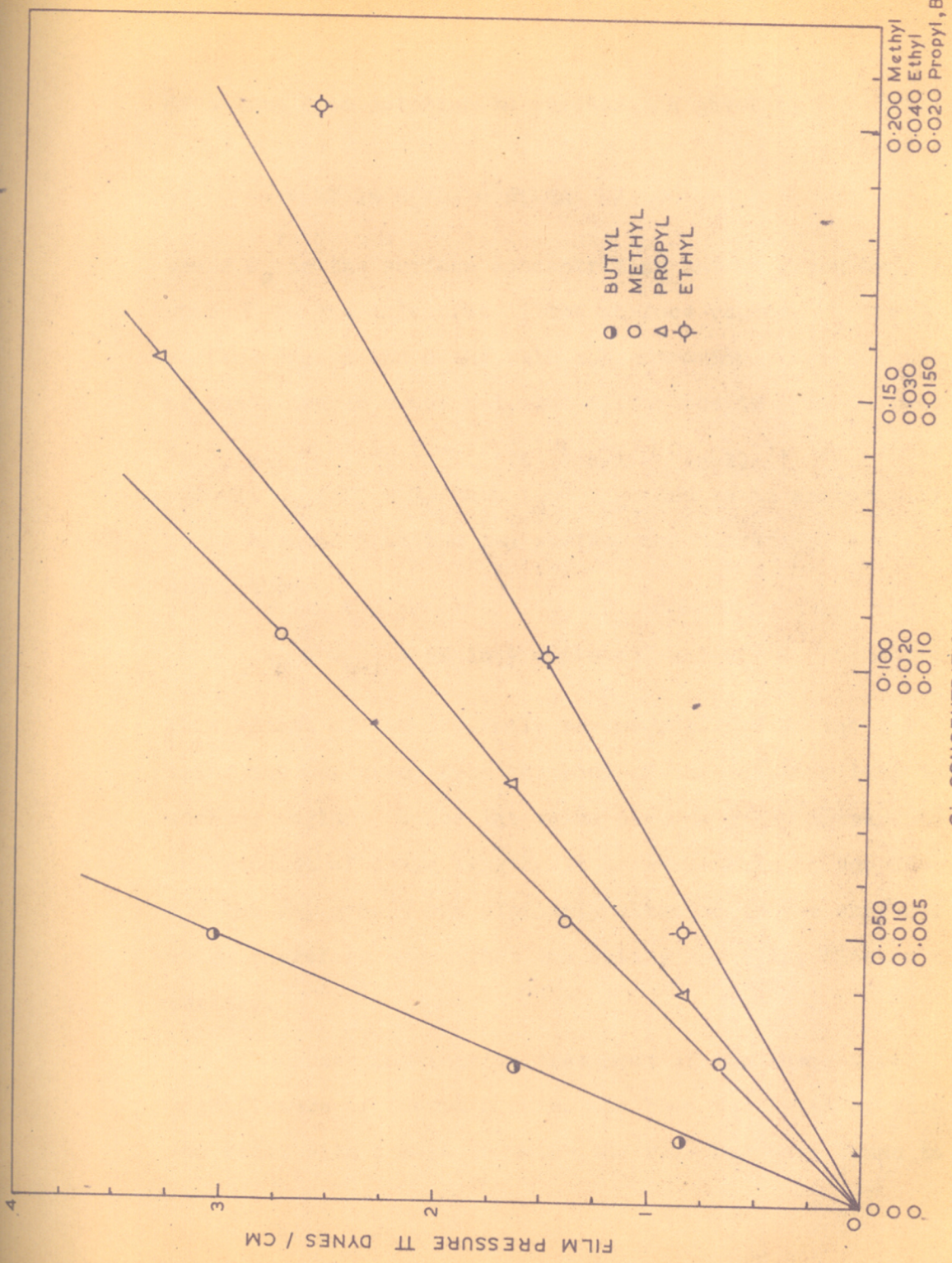


FIG. 1. FILM PRESSURE π AGAINST CONCENTRATION AT 25°C
 ALKYL GLYCOL - WATER SOLUTIONS

of solute from solution to surface, is given by

$$W = RT \ln C_s/C = RT \ln \frac{\delta}{\delta} C$$

where C_s is the surface concentration and is given by $\frac{\delta}{\delta}$ when δ is the thickness of the surface region, δ the surface excess and C the bulk concentration. For solutes of chain length n and $n-1$, the difference in work is then $W_n - W_{n-1} = RT \ln \left(\frac{\delta}{\delta} C_n \right) / \left(\frac{\delta}{\delta} C_{(n-1)} \right)$. By Traube's rule if $C_{n-1}/C_n = 3$, then $\gamma_n = \gamma_{n-1}$ and as an approximation, it is assumed that the two surface concentrations are also the same, then

$$W_n - W_{n-1} = RT \ln 3 = 640 \text{ cal/mole.}$$

This amount of 640 cal./mole may be regarded as the work to bring one CH_2 group from the body of the solution into the surface region. Since the value per CH_2 group appears to be independent of chain length, it is reasonable to suppose that all the CH_2 groups are similarly situated in the surface, which therefore means that the chains are lying flat on the surface.

Another interesting treatment of the theoretical significance of Traube's rule, has been published by Ward³⁹ who dealt with a case in which the rule has been found to

hold fairly well, viz., the effect of a series of fatty acids on the interfacial tension air-water. Ward finds that the conformity of the most reliable of these experimental results to Traube's rule does not in fact prove the frequently stated assumption, which is also regarded as the theoretical basis of the rule that each CH_2 group added to the paraffin chain occupied a similar position to that occupied by the CH_2 groups already present, which would mean that the paraffin chains lie flat along the surface. He concluded instead that the paraffin chains both in the bulk of the solution and in the interface are present in the form of 'most probable spheroids'. The applicability of Traube's rule to the data examined by him is entirely fortuitous due to the fact that the surface areas of the molecules as spheres happen to vary almost linearly with the number of carbon atoms.

Butler pointed out, however, that at the concentrations examined, the surface excess was too great to correspond to the parallel orientation. The perpendicular orientation is thus the more likely one. He considered the major contribution to the free energy of adsorption to be the difference between the free energy of pure solute in the liquid state $(\mu_2^0)_L$ and in dilute solution (μ_2^0) (in the standard state). This difference is related to the solubility for dilute solutions, by the equation

$$(\mu_2^0)_L - \mu_2^0 = RT \ln S$$

where S is the solubility, the limited data available support this view.

An alternative interpretation has been put forward by Aranow and Witten⁴⁰. Each $-\text{CH}_2-$ group added to the molecule has three stable positions of equilibrium, almost equally capable of occupancy. Consequently, the addition of a $-\text{CH}_2-$ group increases the entropy of a gaseous film by $R \ln 3$ and this entropy increase produces the necessary work of adsorption. In the interior of the water the hindered rotations of the hydrocarbon chains are constrained by the neighbouring water molecules, while on the surface the chain protrudes above the surface and hindered rotations are free to occur. If surface behaviour of malonic acid and succinic acid are considered, the energy of adsorption is 1280 cal in the former and 1510 cal in the latter with a difference of 230 cal per $-\text{CH}_2-$ group whereas for long chain hydrocarbons with one polar group it is 620 cal. If the hindered rotation of the $-\text{CH}_2-$ groups are constrained the entropy increase is much less than $R \ln 3$ which is the increase produced by a CH_2 group in molecules attached at one end.

Higgs⁴¹ points out that the free energy per CH_2 group is given by $RT \ln k$ and k is constant at 3, but there is no evidence as to the temperature dependence of k . In the surface layer each $-\text{CH}_2-$ group has not got 3 equal energy

potential minima as assumed by Aranow and Witten, but there is strong reason to believe that two of the minima are at some 600 cal. higher than the third. This would result in a smaller contribution than $R \ln 3$ to the entropy in the surface.

Aranow and Witten⁴² have further discussed the question as to whether the change in free energy when a molecule goes from bulk to surface is due to a difference in the energy of interaction of the hydrocarbon molecule or to an entropy change. The hydrocarbon molecule has a different environment on the surface than it has in the interior.

Traube's rule has an origin primarily from entropy considerations. But this may be due to the molecules of water in the ice-like formation around $-\text{CH}_2-$ group revert to the liquid phase when a $-\text{CH}_2-$ group is taken out of bulk liquid with a corresponding increase in entropy.

The differences between the above views have not yet been resolved.

Recently Lange⁴³ studied the applicability of Traube's rule to nonionic surface active agents of the general formula $\text{C}_n \text{H}_{(2n+1)} (\text{OCH}_2 \cdot \text{CH}_2)_m \text{OH}$. It was qualitatively true upto $n = 12$ i.e. surface activity increased with chain length, but with increase of 'C' beyond 14 surface activity actually

decreased. However his work was done with impure compounds but our data on well purified similar compounds of low molecular weight are in almost quantitative agreement with the rule. Some preliminary work on a related property viz., surface potential, not reported here, also indicate that Traube's rule is quantitatively true in the case of these compounds.

CHAPTER 7

THICKNESS OF ADSORBED LAYER

INTRODUCTION

The interpretation of adsorption isotherm of liquid mixtures is a very controversial subject, with diverse views on the structure and thickness of surface layer. The problem exists for adsorption at any type of interface. The simplest situation is that adsorption is confined to a layer one molecule thick. In many systems the experimental results are compatible with this possibility, but as yet no general method has been advanced which leads to a definite proof. Results which are compatible with adsorption in one molecular layer can as well be interpreted in terms of adsorption spread over two or more molecular layers.

A recent analysis by Nagy and Schay^{44,45} would permit the thickness of the adsorbed layer to be calculated for some types of isotherm if their assumptions are valid. In adsorption by solid adsorbent from two component solutions, the composite isotherm occasionally appears to have a linear section extending over a considerable range of compositions. The equation for adsorption is :

$$\begin{aligned} \frac{n_0 \Delta x}{m} &= n_1^S (1 - x) - n_2^S x \\ &= n_1^S - (n_1^S + n_2^S) x \end{aligned}$$

where n_1^S and n_2^S are the numbers of moles of components 1 and 2, respectively, adsorbed by one g. of solid when in equilibrium with a solution of mole fraction x with respect to component 1. A reduction of mole fraction of Δx occurs, when n_0 moles of the original solution are brought into contact with 'm' g of adsorbent.

Schay's assumption is that $n_0 \Delta x/m$ could vary linearly with respect to x only if n_1^S and n_2^S were constant over that range of concentration i.e. if the adsorbed phase were of constant composition. This is a probable but not the only condition for linearity. Extrapolation of the linear section of the isotherm gives intercepts on the ordinates through $x = 0$ and $x = 1$ of $(n_1^S)_c$ and $-(n_2^S)_c$, respectively which define the composition of the adsorbed phase for this section of the isotherm.

From the monolayer values $(n_1^S)_m$ and $(n_2^S)_m$ i.e. the micromoles of adsorbate required to completely cover the surface area of 1 gm of adsorbent with one molecule thick of adsorbate, the quantity

$$t = \frac{(n_1^S)_c}{(n_1^S)_m} + \frac{(n_2^S)_c}{(n_2^S)_m}$$

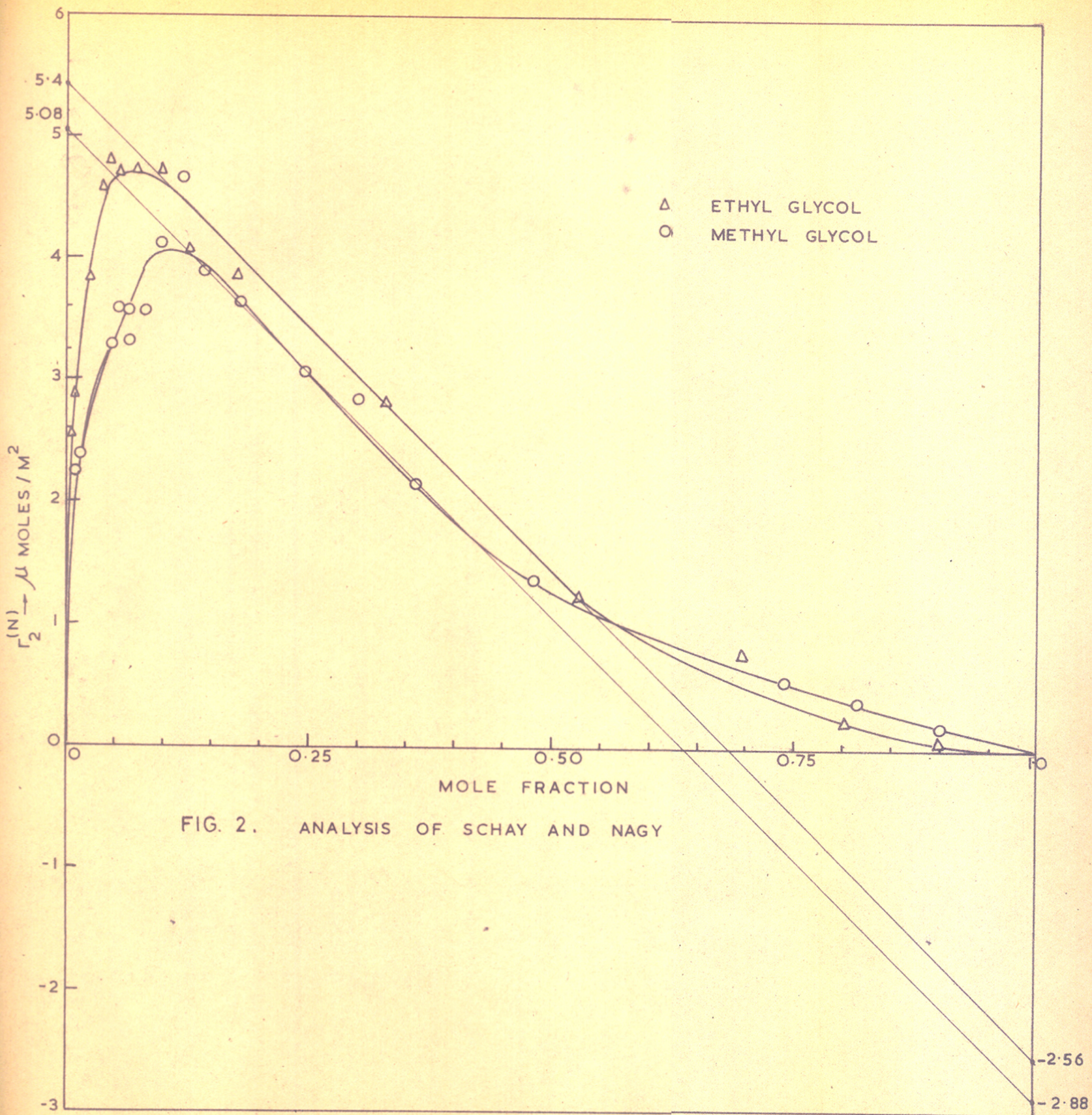
can be calculated, where t is the mean molecular thickness of the adsorbed layer.

The above considerations are not restricted to the solid-liquid interface and can be applied to the liquid-vapour interface also. The surface excess, if calculated according to the Γ_2^N convention, is equivalent to the term $n_0 \Delta x/m$ and the corresponding isotherm can be analysed accordingly.

Very few isotherms of surface excess show a linear or approximately linear section. In what follows we have calculated the thickness of the adsorbed layers of methyl glycol and ethyl glycol - water mixtures at 25°.

The experimental surface tension data were processed with the help of the estimated values of activities noted in Chapter 5. The smoothed surface tension vs. $\log a_2$ curve was divided into very small segments to get $dY/d \log a_2$ values from which the surface excess according to the convention was calculated. The relevant data have been presented in Tables 13 to 16 and graphically in Fig.2. The molecular areas have been assumed to be 10 \AA^2 for water and 28 \AA^2 for glycol ether. For the related alcohols Hommelen²¹ obtained values of the same order.

Haydon and Taylor⁴⁶ also pointed out that $\Delta G\text{-CH}_2\text{-}$ at the oil/water interface is much closer to that for



transference of one $-CH_2-$ group from water to the oil (bulk) phase, than is the value for adsorption at the air/water interface to that for transference from water to the air (bulk) phase. They suggested that the considerable discrepancy in the latter case might be due to the possible folded lying of the hydrocarbon chains, in contact with water. This is more likely with the hydrophilic ether oxygen in the chain of the alkyl glycols and justifies the assumption of a higher area per molecules viz., 28 \AA^2 .

This type of analysis is not possible with n-propyl glycol and n-butyl glycol as the dimensions of these molecules are very much different from that of water.

The region of approximately constant composition may be attributed to the operation of forces between oriented molecules at the interface. The analysis suggests that adsorption is confined to one molecular layer as can be seen in Tables E and F.

TABLE E

Monolayer values for adsorbates calculated

Adsorbent	Adsorbate	$(n_1^s)_m$ μ moles/m ²	Molecular area $\frac{a_2}{A}$ /molecule.
Liquid-vapour interface at 25°	Methyl glycol	5.93	28
	Ethyl glycol	5.93	28
	Water	16.60	10

TABLE F

Adsorbent	Adsorbate	$(n_1^s)_c$ μ moles/m ²	$(n_2^s)_c$ μ moles/m ²	$(n_1^s)_c / (n_1^s)_m$	$(n_2^s)_c / (n_2^s)_m$	$\frac{(n_1^s)_c}{(n_1^s)_m} + \frac{(n_2^s)_c}{(n_2^s)_m}$
Liquid-vapour interface at 25°	Methyl glycol- water	5.08	2.88	0.86	0.17	1.03
	Ethyl-glycol- water	5.40	2.56	0.91	0.15	1.06

TABLE 13

Adsorption at surface of methyl glycol solutions, 25°C

$\log a_2$	$d \log a_2$	dY	$dY/d \log a_2$	Surface excess Γ_1 g. moles/cm ² x 10 ⁻¹⁰	Mole fraction water X_1	Surface excess Γ_N g. moles/cm ² x 10 ⁻¹⁰
3.6847	0.0935	0.50	5.35	0.937	0.9986	0.936
3.7782	0.0969	0.60	6.19	1.085	0.9969	1.081
3.8751	0.1249	1.00	8.01	1.403	0.9959	1.397
2.0000	0.0969	0.95	9.80	1.718	0.9946	1.708
2.0969	0.792	1.00	12.62	2.211	0.9932	2.196
2.1761	0.1249	1.65	13.21	2.314	0.9916	2.295
2.3010	0.0969	1.25	12.89	2.258	0.9870	2.229
2.3979	0.0792	1.10	13.88	2.432	0.9865	2.399
2.4771	0.0670	0.90	13.43	2.353	0.9840	2.315
2.5441	0.0580	0.95	16.38	2.870	0.9810	2.815
2.6021	0.0969	1.60	16.51	2.893	0.9780	2.829
2.6990	0.0792	1.40	17.67	3.076	0.9715	3.008
2.7782	0.0669	1.20	17.93	3.141	0.9650	3.031
2.8451	0.0580	1.00	17.24	3.021	0.9585	2.895
2.9031	0.0511	1.00	19.56	3.427	0.9510	3.259
2.9542	0.0458	1.00	21.83	3.825	0.9440	3.610
1.0000	0.0550	1.20	21.81	3.821	0.9370	3.580

Contd....

Table 13 (Contd.)

$\log a_2$	$d \log a_2$	dY	$dY/d \log a_2$	Surface excess r_1 g.moles/cm ² x 10 ⁻¹⁰	Mole fraction water x_1	Surface excess r_2 g.moles/cm ² x 10 ⁻¹⁰
1.0550	0.0419	0.85	20.29	3.554	0.9340	3.320
1.0969	0.0792	1.75	22.09	3.870	0.9210	3.565
1.1761	0.0669	1.75	26.15	4.582	0.9015	4.152
1.2430	0.0580	1.75	30.17	5.286	0.8800	4.652
1.3010	0.0969	2.50	25.79	4.518	0.8560	3.879
1.3979	0.0792	2.00	25.25	4.424	0.8200	3.628
1.4771	0.0670	1.55	23.13	4.052	0.7560	3.064
1.5441	0.0580	1.35	23.27	4.077	0.7000	2.854
1.6021	0.0969	1.90	19.60	3.434	0.6400	2.198
1.6990	0.0792	1.20	15.15	2.654	0.5200	1.380
1.7782	0.0669	0.90	13.45	2.357	0.4100	0.966
1.8451	0.0580	0.70	12.07	2.114	0.2600	0.549
1.9031	0.0511	0.60	11.74	2.057	0.1840	0.379
1.9542	0.0458	0.50	10.92	1.913	0.1000	0.193
0.0000	-	-	-	-	0.0000	-

TABLE 14

Adsorption at surface of ethyl glycol solutions, 25°C

log a ₂	dlog a ₂	dY	dY/dlog a ₂	Surface excess $\Gamma_1^2 \times 10^{-10}$ g.moles/cm ²	Mole fraction water x ₁	Surface excess $\Gamma_N^2 \times 10^{-10}$ g.moles/cm ²
3.6021	0.0969	0.50	5.159	0.904	0.9991	0.903
3.6990	0.0792	0.50	6.313	1.106	0.9989	1.106
3.7782	0.0969	0.90	9.287	1.627	0.9987	1.625
3.8751	0.1249	1.30	10.41	1.824	0.9982	1.820
2.0000	0.0969	1.60	16.51	2.893	0.9976	2.886
2.0969	0.0792	0.90	11.36	1.991	0.9971	1.985
2.1761	0.1249	1.55	12.41	2.174	0.9965	2.167
2.3010	0.0969	1.25	12.89	2.258	0.9960	2.249
2.3979	0.0792	1.55	19.57	3.429	0.9945	3.410
2.4771	0.0670	0.90	13.43	2.353	0.9935	2.338
2.5441	0.0580	0.85	14.66	2.568	0.9925	2.548
2.6021	0.0969	1.60	16.51	2.893	0.9910	2.867
2.6990	0.0792	1.40	17.67	3.096	0.9885	3.060
2.7782	0.0669	1.25	18.68	3.273	0.9860	3.227
2.8451	0.0580	1.05	18.10	3.171	0.9840	3.120
2.9031	0.0511	1.50	29.35	5.142	0.9815	5.047

Contd....

Table 14 (Contd..)

log a ₂	dlog a ₂	dY	dY/dlog a ₂	Surface excess Γ_2 g.moles/cm ² x 10 ⁻¹⁰	Mole fraction water x ₁	Surface excess Γ_N g.moles/cm ² x 10 ⁻¹⁰
2.9542	0.0458	1.00	21.83	3.825	0.9790	3.744
1.0000	0.0550	1.25	22.72	3.981	0.9760	3.885
1.0550	0.0419	1.10	26.25	4.599	0.9735	4.477
1.0969	0.0792	2.05	2.588	4.554	0.9695	4.396
1.1761	0.0669	1.75	26.15	4.582	0.9620	4.407
1.2430	0.0580	1.60	27.58	4.832	0.955	4.615
1.3010	0.0969	2.60	26.83	4.700	0.9460	4.446
1.3979	0.0792	2.30	29.04	5.088	0.9270	4.716
1.4771	0.0670	2.00	29.85	5.230	0.9020	4.717
1.5441	0.0580	1.55	26.72	4.681	0.8740	4.092
1.6021	0.0969	2.60	26.83	4.701	0.8260	3.883
1.6990	0.0792	1.90	23.98	4.201	0.6700	2.815
1.7782	0.0669	1.00	14.94	2.618	0.4700	1.230
1.8451	0.0580	0.80	13.79	2.417	0.3140	0.759
1.9031	0.0511	0.30	5.870	1.028	0.2000	0.206
1.9542	0.0458	0.20	4.37	0.765	0.1020	0.078

TABLE 15

Adsorption at the surface of n-propyl glycol solutions, 25°C

log a ₂	dlog a ₂	dY	dY/dlog a ₂	Surface excess $\frac{\Gamma_1}{\Gamma_2} \times 10^{-10}$ g. moles/cm ²	Mole fraction water $\times 10^4$	Surface excess $\frac{\Gamma_1}{\Gamma_2} \times 10^{-10}$ g. moles/cm ²
3.5647	0.0374	0.20	5.347	0.937	0.9997	0.937
3.6021	0.0969	0.60	6.191	1.085	0.9997	1.084
3.6990	0.0792	0.55	6.944	1.217	0.9976	1.216
3.7782	0.0969	0.80	8.255	1.446	0.9996	1.445
3.8751	0.1249	1.40	11.208	1.964	0.9994	1.962
2.0000	0.0969	1.30	13.410	2.349	0.9993	2.348
2.0969	0.0792	1.20	15.150	2.654	0.9990	2.651
2.1761	0.1249	1.80	14.411	2.525	0.9988	2.522
2.3010	0.0969	1.45	14.960	2.621	0.9985	2.617
2.3979	0.0792	1.30	16.41	2.875	0.9982	2.870
2.4771	0.0670	1.20	17.91	3.138	0.9980	3.132
2.5441	0.0580	1.00	17.24	3.021	0.9975	3.013
2.6021	0.0969	1.70	17.54	3.073	0.9975	3.065
2.6990	0.0792	1.50	18.93	3.317	0.9970	3.307
2.7782	0.0669	1.50	22.42	3.928	0.9960	3.912
2.8451	0.0580	1.20	20.68	3.623	0.9950	3.605
2.9031	0.0511	1.05	20.54	3.599	0.9940	3.577
2.9542	0.0458	1.10	24.01	4.207	0.9930	4.177

Contd..

Table 15 (Contd.)

log a ₂	dlog a ₂	dY	dY/dlog a ₂	Surface excess Γ_1 g.moles/cm ² x 10 ⁻¹⁰	Mole fraction water x ₁	Surface excess Γ_2 g.moles/cm ² x 10 ⁻¹⁰
1.0000	0.0550	1.25	22.72	3.981	0.9925	3.951
1.0550	0.0419	1.00	23.86	4.180	0.9908	4.142
1.0969	0.0792	2.00	25.25	4.420	0.9900	4.380
1.1761	0.0669	1.65	24.66	4.320	0.9875	4.266
1.2430	0.0580	1.40	24.13	4.228	0.9850	4.164
1.3010	0.0969	2.40	24.76	4.338	0.9825	4.262
1.3979	0.0792	1.70	21.46	3.760	0.9780	3.677
1.4771	0.0670	1.40	20.89	3.660	0.9710	3.554
1.5441	0.0580	1.20	20.68	3.623	0.9650	3.496
1.6021	0.0969	1.80	18.57	3.254	0.9590	3.120
1.6990	0.0792	1.30	16.41	2.875	0.9420	2.708
1.7782	0.0669	0.65	9.72	1.702	0.9175	1.562
1.8451	0.0580	0.40	6.896	1.208	0.8780	1.061
1.9031	0.0511	0.18	3.424	0.600	0.2360	0.142
1.9542	0.0238	0.10	0.420	0.734	0.1000	0.074

TABLE 16

Adsorption at surface of n-butyl glycol solutions, 25°C

log a ₂	dlog a ₂	dY	dY/dlog a ₂	Surface excess Γ_1 g. moles/cm ² x 10 ⁻¹⁰	Mole fraction water X ₁	Surface excess Γ_2 g. moles/cm ² x 10 ⁻¹⁰
1.0550	0.0415	0.80	19.09		0.9979	
1.0560	0.0420	1.00	24.72		0.9978	
2.0000	0.0969	1.15	11.86	2.08	0.9998	2.078
2.0969	0.0792	0.90	11.36	1.990	0.9998	1.990
2.1761	0.1249	1.55	12.41	2.174	0.9998	2.174
2.3010	0.0969	1.25	12.89	2.258	0.9997	2.257
2.3979	0.0792	1.20	15.15	2.654	0.9996	2.653
2.4771	0.0670	1.10	16.41	2.875	0.9995	2.874
2.5441	0.0580	1.00	17.24	3.020	0.9994	3.018
2.6021	0.0969	1.85	19.09	3.345	0.9993	3.343
2.6990	0.0792	1.70	21.46	3.760	0.9992	3.757
2.7782	0.0661	1.40	20.92	3.665	0.9989	3.661
2.8451	0.0580	1.28	22.06	3.865	0.9988	3.860
2.9031	0.0511	1.10	21.52	3.770	0.9986	3.765
2.9542	0.0458	1.10	24.01	4.207	0.9984	4.200
3.0000	0.0550	1.20	21.81	3.821	0.9982	3.814

Contd...

Table 16 (Contd..)

log a ₂	dlog a ₂	dY	dY/dlog a ₂	Surface excess Γ_1 g.moles/cm ² x 10 ⁻¹⁰	Mole fraction water x ₁	Surface excess Γ_N g.moles/cm ² x 10 ⁻¹⁰
1.0550	0.0419	0.80	19.09	3.345	0.9979	3.338
1.0969	0.0792	1.80	22.72	3.981	0.9977	3.972
1.1761	0.0669	1.40	20.92	3.665	0.9972	3.655
1.2430	0.0580	1.25	21.55	3.776	0.9967	3.764
1.3010	0.0969	2.10	21.67	3.797	0.9962	3.783
1.3979	0.0792	1.95	24.62	4.313	0.9953	4.294
1.4771	0.0670	1.65	24.62	4.313	0.9942	4.288
1.5441	0.0580	1.50	25.86	4.531	0.9932	4.500
1.6021	0.0969	2.70	27.86	4.881	0.9922	4.843
1.6990	0.0792	2.15	27.14	4.755	0.9898	4.706
1.7782	0.0669	1.50	22.42	3.928	0.9874	3.879
1.8451	0.0580	1.00	17.24	3.021	0.9851	2.976
1.9031	0.0369	0.50	13.55	2.374	0.9823	2.332
1.9400	0.0520	0.42	8.08	1.415	0.9800	1.387
1.9920	0.0480	0.20	4.17	0.730	0.9764	0.713

CHAPTER 8

INDIVIDUAL ISOTHERMS

INTRODUCTION

The structure of the surface layer of solutions continues to be of interest. For systems in which the components are completely miscible neither can be regarded as solvent or as solute over the whole range of concentration. It thus becomes important to recognize that each component of a mixture may be adsorbed and it would be of interest to know their extents over a wide range of compositions. Once the surface excess has been calculated as described earlier, it is possible to obtain the actual surface concentrations for each component. This process corresponds to resolving the composite isotherm for adsorption into individual isotherms. The surface concentrations unlike those of surface excess cannot be calculated from purely thermodynamic data. Three assumptions will have to be made (a) as to the orientation of the adsorbed molecules at the interface, (b) the area which they occupy and (c) whether the adsorbed layer is monomolecular or multimolecular. For vapour/solution interface, there is no subsidiary evidence as to the likely orientation of the molecules such as is given

for liquid-solid interface, by considering adsorption of the individual vapours by the solids. The value of the analysis therefore depends on the soundness with which orientation and molecular areas are judged.

Harkins and Wampler⁴⁷ used the Gibb's equation to calculate the surface excess of n-butyl alcohol-water system, expressed in terms of Γ_2^i . By adding the number of butyl alcohol molecules which would be present if there were no surface excess they obtained the total number present in a unit area of the surface. The number of butyl alcohol molecules present in a unit area of the surface, if there were no adsorption, was assumed to be the two-thirds power of the number present in 1 c.c. of solution.

Butler⁴⁸ claimed that this assumption in general was an over-estimate and pointed out that

$$\Gamma_2 = \Gamma_2^i + \frac{x_2}{x_1} \Gamma_1$$

where Γ_2 and Γ_1 are numbers of moles of solute and solvent per unit area of the surface and x_2 and x_1 are respectively the mole fraction of solute and solvent in the bulk phase.

An evaluation of Γ_2 and Γ_1 can be obtained more simply by using equation (1) and (2)

$$\Gamma_2^N = x_1 \Gamma_2 - x_2 \Gamma_1 \quad \dots (1)$$

$$\Gamma_1 A_1 + \Gamma_2 A_2 = 1 \quad \dots (2)$$

where A_1 and A_2 are the areas occupied by a mole of water in the unimolecular layer and by a mole of solute respectively. A direct use of the equation (1) avoids the need for corrections and is valid for all concentrations. By solving equation (1) and (2) simultaneously we obtain equations (3) and (4)

$$\bar{\Gamma}_2 = \frac{A_1 \bar{\Gamma}_2^N + x_2}{x_1 A_1 + x_2 A_2} \quad \dots (3)$$

$$\bar{\Gamma}_1 = \frac{A_2 \bar{\Gamma}_1^N + x_1}{x_1 A_1 + x_2 A_2} \quad \dots (4)$$

The values for alkyl glycols calculated are shown in Tables 17 to 20 and plotted in units of μ moles/sq.cm. in Figs. 3 and 4. The molecular areas were assumed to be 18.4 \AA^2 for the solutes and 10 \AA^2 for water.

DISCUSSION

The reason for assuming the above value for the area of solute is that the use of models show that the hydroxyl group does not project beyond the boundaries of the hydrocarbon chain, which in crystals has a cross sectional area of 18.4 \AA^2 . Deo⁴⁹ and others working on insoluble monolayers of alkyl glycols found no difference in areas between the alcohols and alkyl glycols.

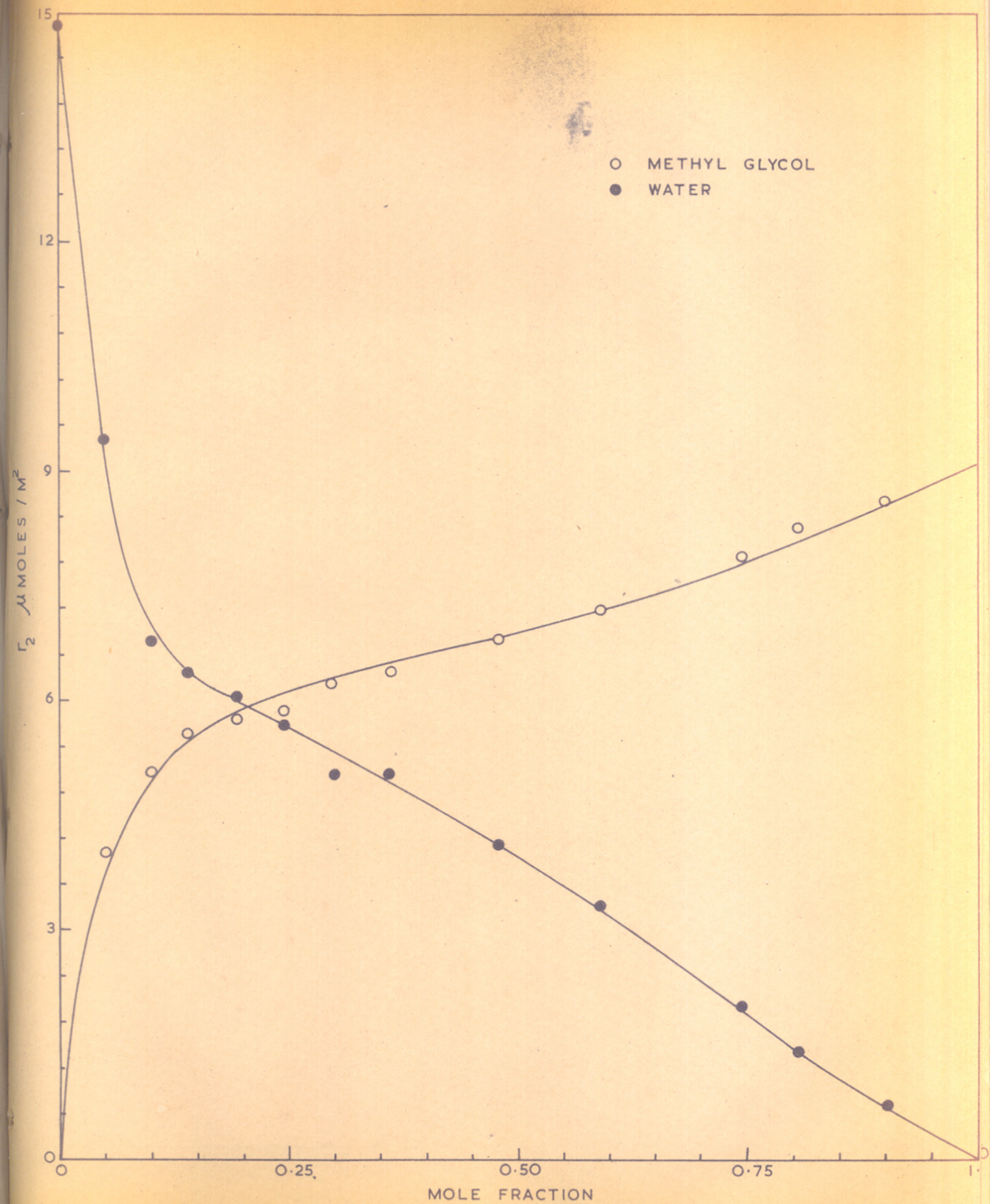


FIG. 3. INDIVIDUAL ISOTHERMS
 METHYL GLYCOL-WATER

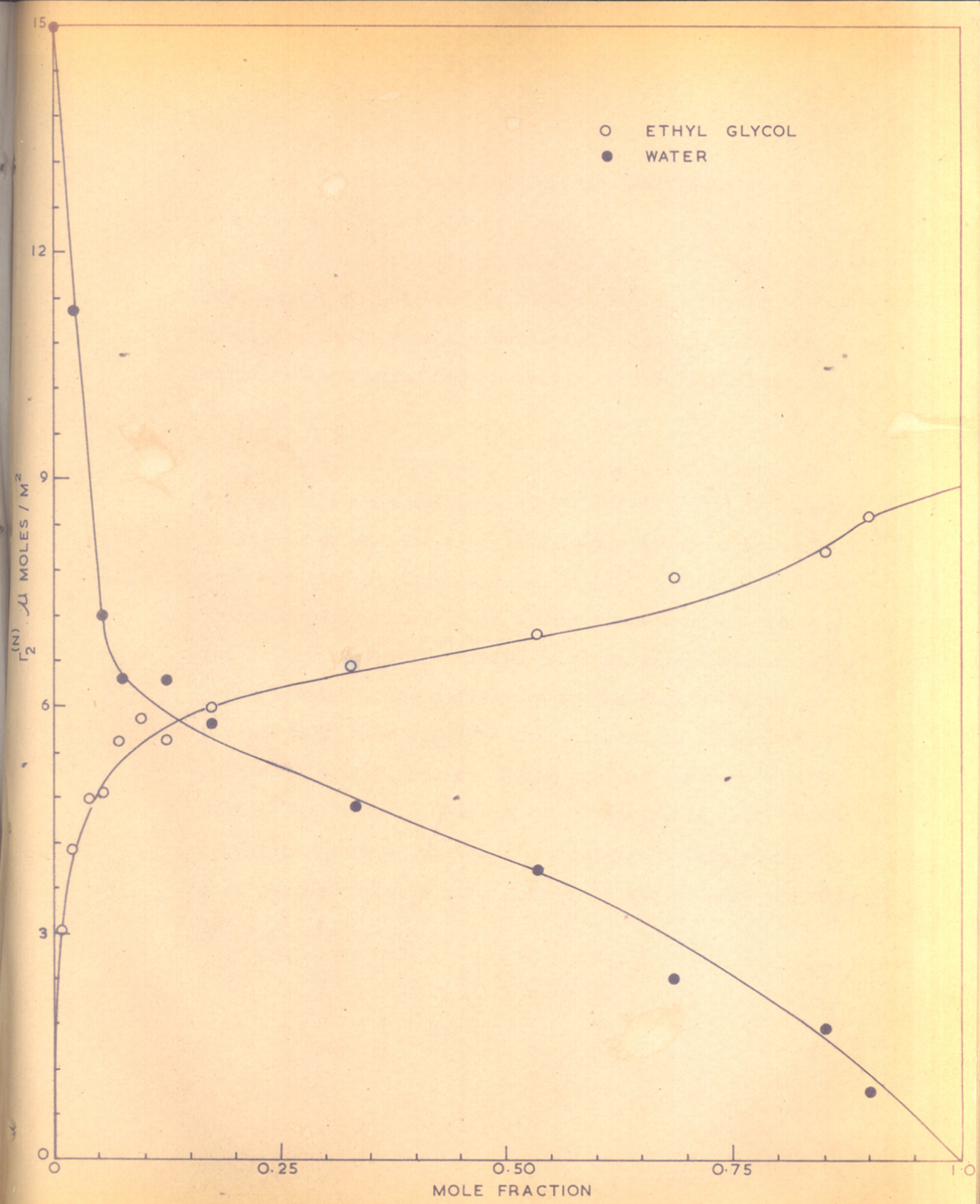


FIG. 4. INDIVIDUAL ISOTHERMS
 ETHYL GLYCOL - WATER

For the first two members, the individual isotherms are similar to that of the alcohols. A complete monolayer is formed only from the pure component. The propyl and butyl derivatives do not seem to behave like the corresponding alcohols but this is not surprising when one considers the complications which may arise due to micellization phenomenon.

Possible criticisms of the above calculations are that no allowance has been made for difference in length of molecules and the co-area/molecule found by us as 28.0 \AA^2 from equation of state and not 18.4 \AA^2 . Kipling⁵⁰ found that for butyl alcohol and higher members of the series (molecular size of the order of alkyl glycol ethers under consideration), the difference in the lengths of water and alcohol molecules affected the calculation of number of solute molecules present in the surface layer to a very negligible extent. However, it is desirable that, for comparison purpose at least, calculations with 28.0 \AA^2 area per molecule of glycol ether should be made and this is under progress.

TABLE 17

Methyl glycol-water : Composition of the surface layer

Mole fraction x_2	Surface concentration	
	Γ_2	Γ_1
	$\mu \text{ moles/m}^2$	
0.001	0.96	14.84
0.003	1.13	14.52
0.004	1.46	13.91
0.005	1.80	13.29
0.007	2.30	12.37
0.008	2.42	12.15
0.013	2.42	12.15
0.016	2.31	12.34
0.019	3.08	10.93
0.022	3.14	10.83
0.028	3.40	10.31
0.035	3.51	10.14
0.042	3.47	10.22
0.049	3.91	9.40
0.056	4.33	8.62
0.063	4.39	8.52
0.066	4.18	8.90

Contd....

Table 17 (Contd..)

Mole fraction x_2	Surface concentration	
	Γ_2	Γ_1
	μ moles/m ²	
0.079	4.57	8.19
0.098	5.33	6.80
0.120	6.04	5.49
0.142	5.57	6.36
0.180	5.75	6.02
0.244	5.91	5.72
0.300	6.26	5.08
0.360	6.28	5.05
0.480	6.78	4.13
0.590	7.19	3.36
0.740	7.91	2.04
0.816	8.27	1.40
0.900	8.63	0.74

TABLE 18

Ethyl glycol-water : Composition of the surface layer

Mole fraction x_2	Surface concentration	
	\bar{r}_2	\bar{r}_1
	μ moles/m ²	
0.0009	0.92	14.91
0.0011	1.11	14.55
0.0013	1.65	13.57
0.0021	1.84	13.21
0.0031	2.02	12.88
0.0040	2.21	12.53
0.0041	2.30	12.37
0.0061	3.48	10.19
0.0071	2.43	12.13
0.0081	2.65	11.72
0.0090	2.99	11.10
0.0120	3.22	10.67
0.0140	3.41	10.32
0.0160	3.39	10.45
0.0185	5.27	6.90
0.210	4.02	9.20
0.240	4.19	8.89

Contd..

Table 18 (Contd.)

mole fraction x_2	Surface concentration	
	Γ_2	Γ_1
	$\mu \text{ moles/m}^2$	
0.0265	4.79	7.79
0.0305	4.77	7.82
0.0380	4.88	7.62
0.0450	5.16	7.10
0.0540	5.11	7.20
0.0730	5.58	6.33
0.0980	5.85	5.83
0.1260	5.58	6.33
0.1740	5.90	5.74
0.3300	6.49	4.66
0.5300	6.94	3.83
0.6860	7.71	2.41
0.8000	8.07	1.76
0.8980	8.50	0.96

TABLE 19

n-propyl glycol-water : Composition of the surface layer

Mole fraction x_2	Surface concentration	
	Γ_2	Γ_1
	$\mu\text{ moles/m}^2$	
0.0003	0.94	14.87
0.0003	1.08	14.60
0.0004	1.22	14.35
0.0004	1.45	13.92
0.0006	1.97	12.87
0.0007	1.69	13.49
0.0010	2.66	11.70
0.0012	2.53	11.84
0.0015	2.63	11.76
0.0018	2.90	11.26
0.0020	3.15	10.80
0.0025	3.04	11.00
0.0025	3.10	10.89
0.0030	3.34	10.45
0.0040	3.96	9.31
0.0050	3.67	9.85

Contd...

Table 19 (Contd.)

Mole fraction x_2	Surface concentration	
	Γ_2	Γ_1
	$\mu \text{ moles}/\mu^2$	
0.0060	3.65	9.88
0.0070	4.26	8.76
0.0075	4.04	9.16
0.0092	4.26	8.76
0.0100	4.58	8.17
0.0125	4.41	8.48
0.0150	4.35	8.59
0.0175	4.48	8.35
0.0220	3.97	9.29
0.0290	3.94	9.35
0.0350	3.96	9.31
0.0410	3.67	9.85
0.0580	3.50	10.16
0.0825	2.74	11.56

TABLE 20

n-butyl glycol-water : Composition of the surface layer

Mole fraction x_2	Surface concentration	
	Γ_2	Γ_1
	μ moles/m ²	
0.0002	2.08	12.77
0.0002	3.30	10.53
0.0002	2.17	12.60
0.0003	2.26	12.44
0.0004	2.65	11.72
0.0005	2.88	11.30
0.0006	3.02	11.04
0.0007	3.35	10.43
0.0008	3.76	9.68
0.0011	3.67	9.85
0.0012	3.87	9.48
0.0014	3.78	9.64
0.0016	4.22	8.83
0.0018	3.83	9.55
0.0021	3.37	10.40
0.0023	4.01	9.22

Contd...

Table 20 (Contd.)

Mole fraction x_2	Surface concentration	
	Γ_2	Γ_1
	$\mu \text{ moles/m}^2$	
0.0028	3.69	9.81
0.0033	3.80	9.61
0.0038	3.83	9.55
0.0047	4.35	8.59
0.0058	4.36	8.58
0.0068	4.58	8.17
0.0078	4.94	7.51
0.0102	4.83	7.71

CHAPTER 9

EQUATIONS OF STATE

INTRODUCTION

As in the case of ordinary three dimensional matter, the gaseous state concept of adsorbed monolayers is simple. The molecules are floating about in the surface layer for enough apart so that they exert relatively little force on one another. The interpretation of the film pressure-area (π -A) behaviour of gaseous monolayers has followed a two dimensional kinetic analysis, corresponding to the three dimensional ideal gas theory and ignoring the subphase liquid. This approach assumes that the molecules of the film move about with average translational kinetic energy of $1/2 kT$ for each degree of freedom. The two dimensions in the plane of the surface lead to a total kinetic energy of kT , which is assumed to produce the surface pressure, and this leads to an ideal two dimensional gas equation.

$$\pi A = kT$$

The kinetic analysis of monolayer ideal gas behaviour which ignores the subphase liquid molecules is open to considerable criticism. The experimental realization of

the ideal equation of state is difficult. Fowkes⁵¹ pointed out that the approximation required in deriving the ideal expression lead to appreciable errors at surface pressures as low as 1 dyne/cm. Various attempts have been made to allow for such 'imperfect gas' behaviour although none of them is entirely satisfactory. It is obvious that finite size of the film forming molecules themselves is an important source of deviation, since both the kinetic and thermodynamic derivation of equation $\pi A = kT$ require that a negligible fraction of the actual surface be occupied by the molecules. Since it is probable that the molecules lie flat in a gaseous monolayer at a liquid-gas interface, an area of the order of 50 \AA^2 , may well be physically taken up by each molecule. Attempts have been made to allow for this effect by introducing an excluded or coarea term and writing equation

$$\pi (A - A_0) = kT$$

with A_0 being considered either an adjustable parameter or being associated with the observed molecular area in condensed films. This type of equation has found some success in fitting data for films at oil-water interfaces⁵². It is found in practice, that deviations for electrolytically neutral monolayer are invariably negative at lowest pressures while equation $\pi(A - A_0) = kT$ would require that πA be greater than kT . Such evidence of nonideality has been

ascribed to attractive force between the film forming molecules, by analogy with van der Waals treatment of imperfect 3-dimensional gases.

Various expressions have been proposed to allow for the negative deviations of the π -A product from the ideal value. For example, Schofield and Rideal⁵³ used an equation of the following form

$$\pi(A - A_0) = q kT$$

where q is less than unity (typically about 0.7). Combination of the equation $\pi(A - A_0) = q kT$ with the Gibbs adsorption equation, followed by integration, leads to the results⁵⁴

$$\ln \pi' = \frac{\pi A_0}{kT} + q \ln \pi$$

where π' is the pressure the film would have if it were perfectly gaseous. An application of this equation to the experimental results enables A_0 and q to be determined. A plot of $\log_{10} \pi'/\pi$ against $\log_{10} \pi/\pi$ should be straight line with a slope q and an intercept on the $\log_{10} \pi'/\pi$ axis of $A_0/2.303 kT$. π' is equal to $C \times \alpha$ being obtained from the initial linear port of the π vs. C curve.

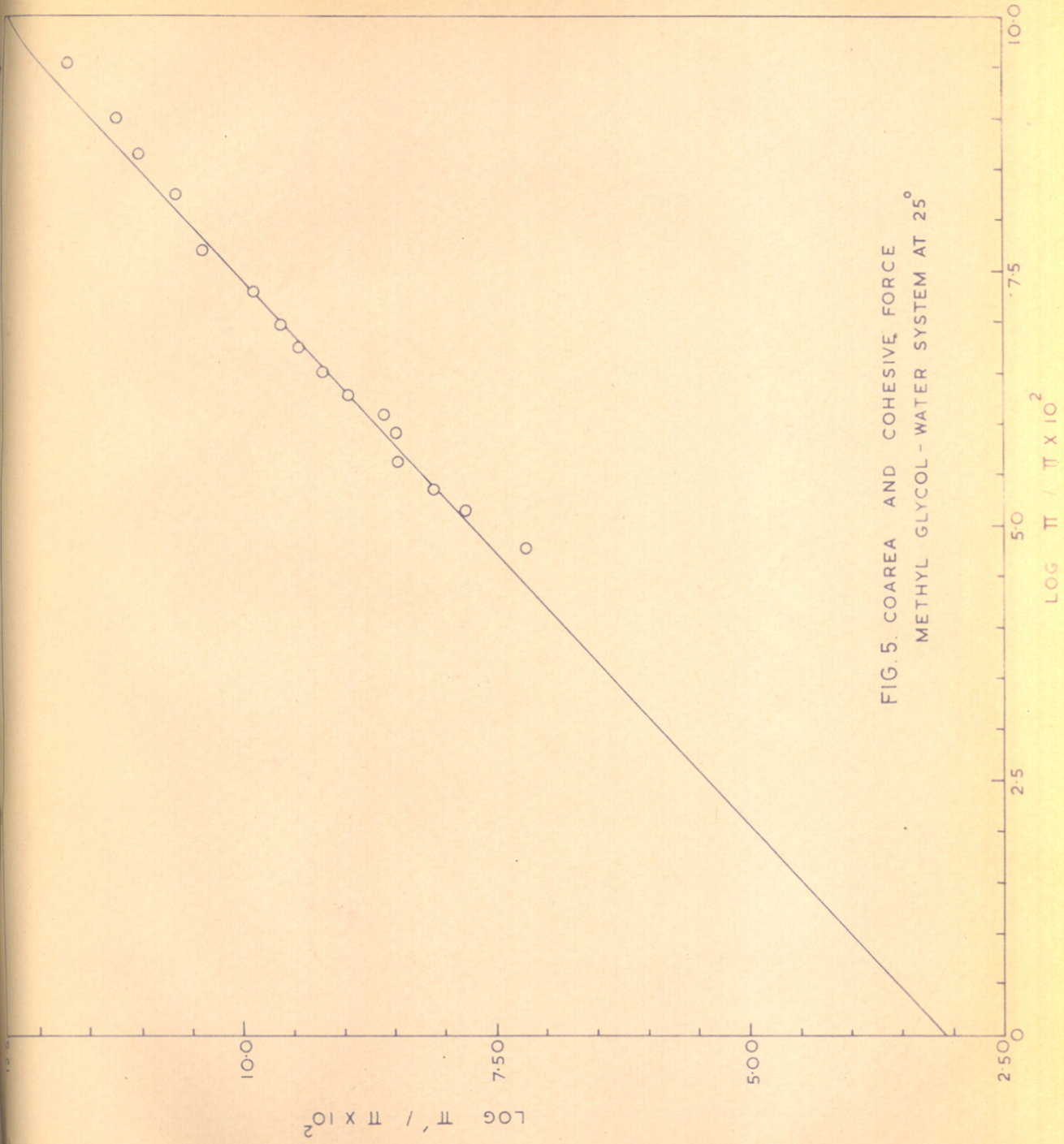


FIG 5. COAREA AND COHESIVE FORCE
METHYL GLYCOL - WATER SYSTEM AT 25°

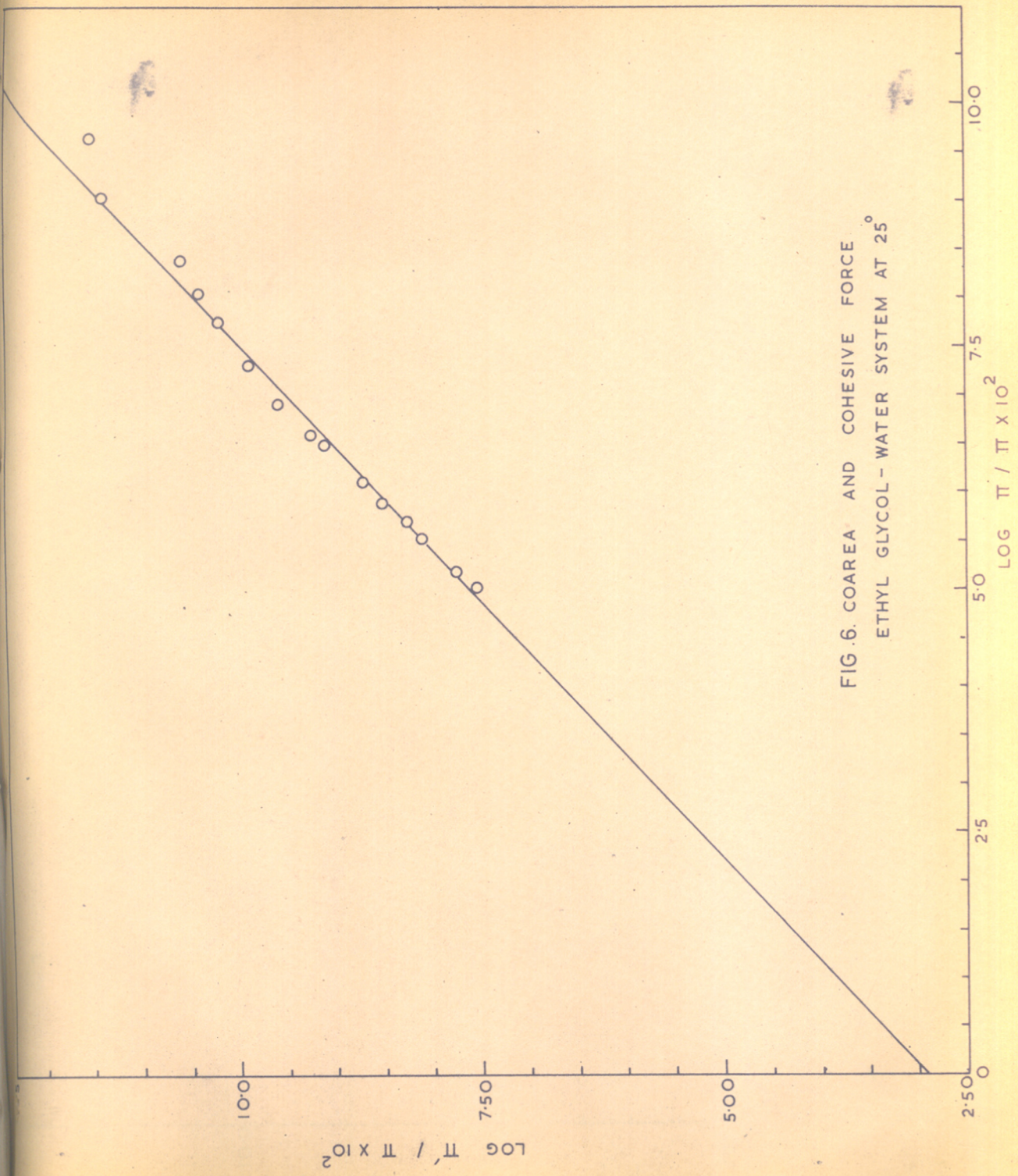


FIG. 6. COAREA AND COHESIVE FORCE
 ETHYL GLYCOL - WATER SYSTEM AT 25°

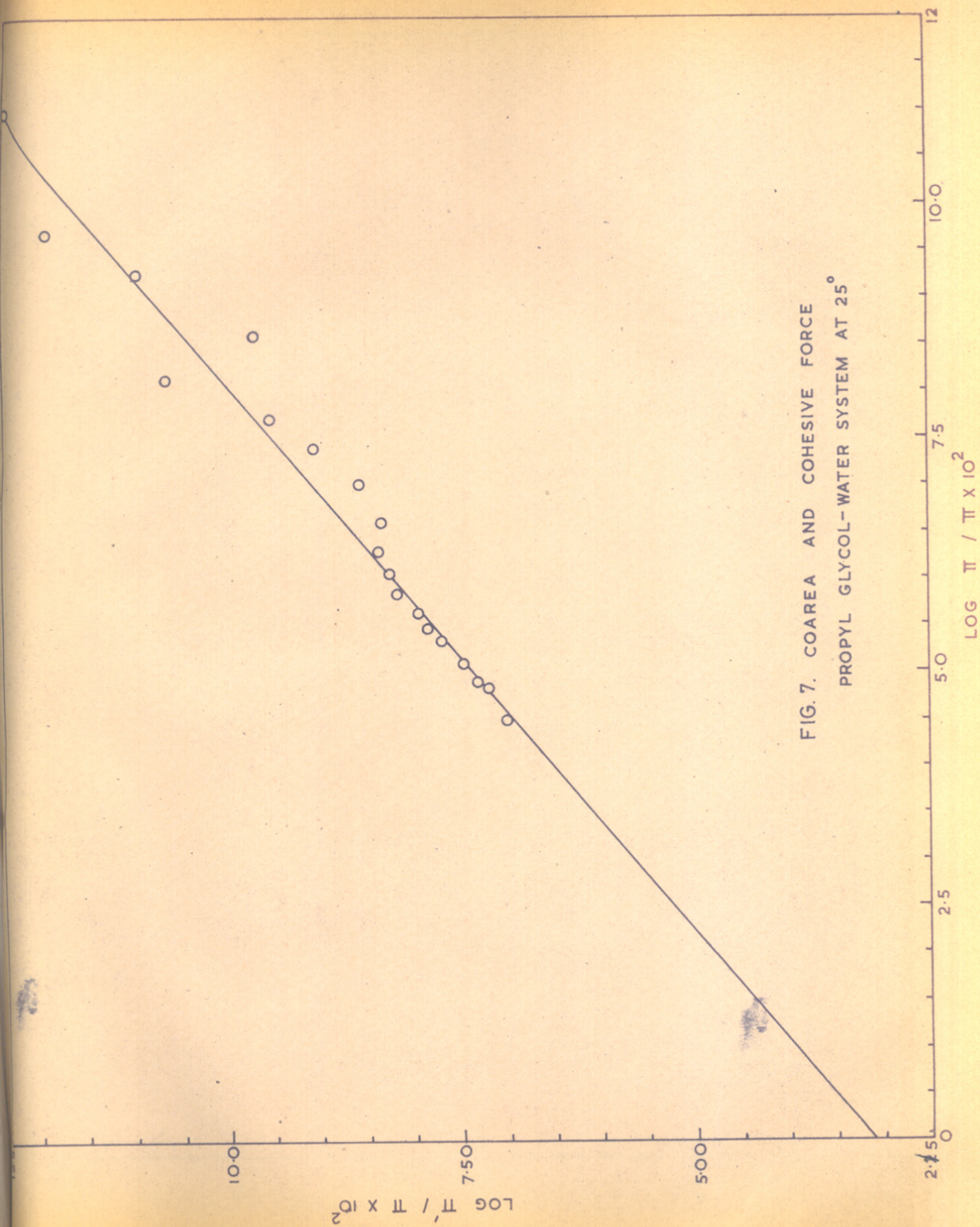


FIG. 7. COAREA AND COHESIVE FORCE
 PROPYL GLYCOL-WATER SYSTEM AT 25°

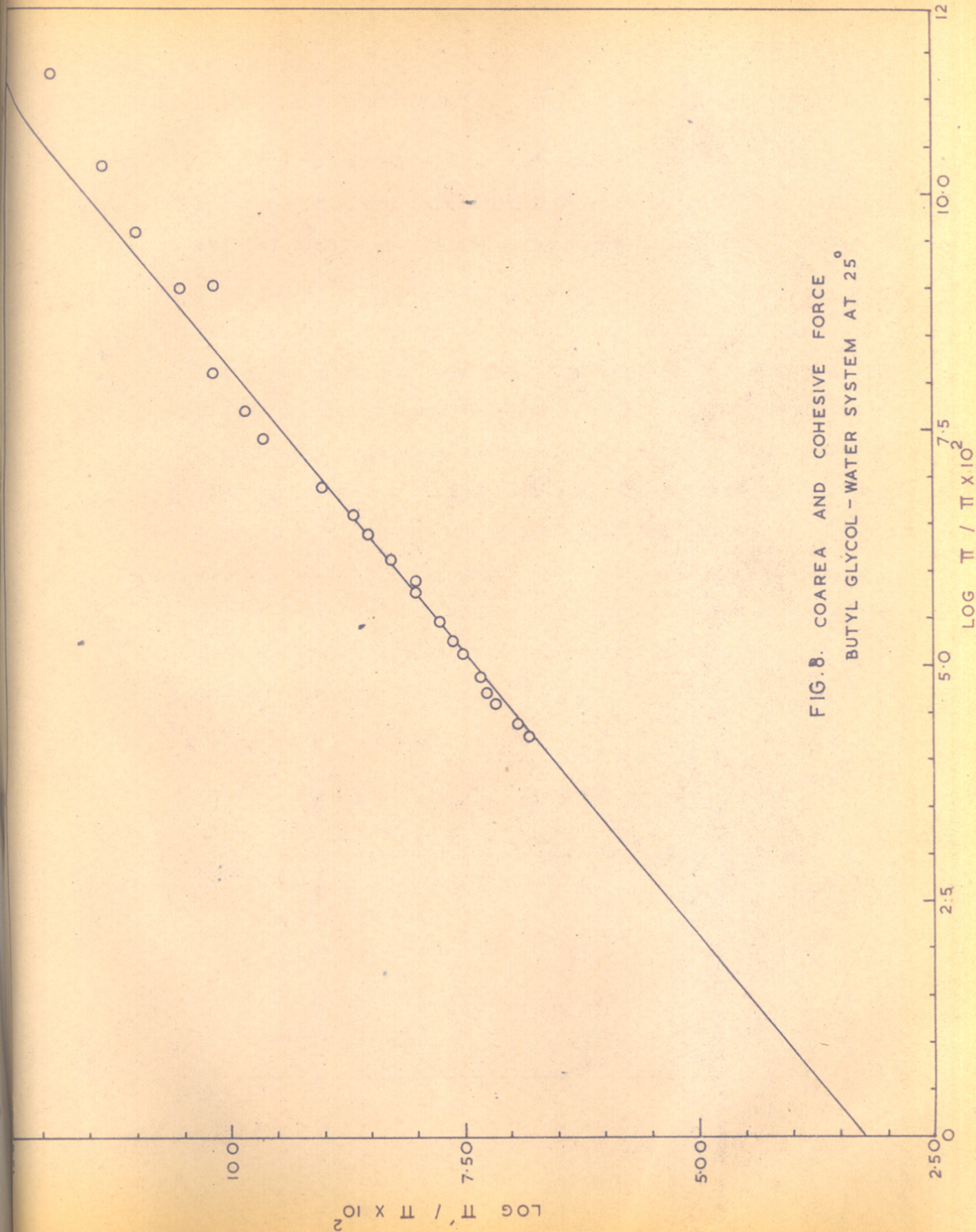


FIG. 8. COAREA AND COHESIVE FORCE
 BUTYL GLYCOL - WATER SYSTEM AT 25°

RESULTS AND DISCUSSION

The values of π' and π for alkyl glycols as calculated from the data are tabulated in Tables 21 to 24. α values are the Traube coefficients taken from Chapter 6. Plots of $\frac{\log \pi'}{\pi}$ vs $\frac{\log \pi}{\pi}$ are given in Figs. 5 to 8. The Table G gives values of q and A_0 for alkyl glycols. The value of the slope q goes on decreasing indicating an increased cohesive force between molecules as the chain length is increased. The cohesive forces are not very much different from those of the corresponding alcohols taking -O- (ether oxygen) equal to one CH_2 group. But the coarea per molecule appears to be higher, probably due to hydrocarbon chains partly lying in an inclined zigzag form on the water surface. Such a possibility has been suggested in case of alcohols at the air-water interface⁴⁶.

Table - G

Values of q and A_0 of alkyl glycols at 25°

	q	A_0
Methyl glycol	0.95	28.5
Ethyl glycol	0.94	28.5
Propyl glycol	0.85	28.5
Butyl glycol	0.78	30.8

TABLE 21

Equation of state : Methyl glycol-water, 25°C

 $\alpha = 26$, dynes/cm/mol/l

Molarity C	Film pressure π dynes/cm.	$\log \pi$	$(\log \pi / \pi) 10^2$	$\pi' = \alpha c$	$\log \pi'$	$(\log \pi' / \pi) 10^2$
0.077	3.90	0.5911	15.15	2.05	0.3118	7.98
0.181	4.40	0.6435	14.60	4.70	0.6721	15.29
0.224	5.00	0.6990	13.99	5.83	0.7657	15.31
0.299	6.00	0.7782	13.00	7.77	0.8904	14.82
0.369	6.95	0.8420	12.10	9.60	0.9823	14.12
0.454	7.95	0.9004	11.30	11.80	1.0719	13.48
0.693	9.60	0.9823	10.22	18.00	1.2553	13.06
0.717	10.55	1.0355	9.55	18.65	1.2707	11.70
0.844	11.95	1.0771	9.02	21.90	1.3404	11.22
0.994	12.85	1.1089	8.64	25.80	1.4116	11.00
1.136	13.80	1.1399	8.25	29.50	1.4698	10.65

Contd....

Table 21 (Contd.)

Molarity c	Film pressure π dynes/cm.	$\log \pi$	$(\log \pi / \pi) 10^2$	$\pi' = ac$	$\log \pi'$	$(\log \pi' / \pi') 10^2$
1.445	15.40	1.1875	7.71	36.6	1.5752	10.42
1.750	16.80	1.2253	7.30	45.5	1.6580	9.88
2.040	18.00	1.2553	6.96	53.0	1.7243	9.60
2.350	19.00	1.2788	6.75	61.00	1.7853	9.40
2.630	20.00	1.3010	6.50	68.4	1.8351	9.18
2.920	21.00	1.3222	6.30	76.0	1.8805	8.95
3.02	22.20	1.3464	6.12	78.5	1.8949	8.61
3.47	23.05	1.3626	5.91	90.2	1.9552	8.42
4.15	24.80	1.3945	5.62	108.0	2.0334	8.45
4.74	26.55	1.4240	5.36	123.2	2.0906	8.10
5.40	28.30	1.4518	5.14	140.5	2.1476	7.80
6.31	30.80	1.4886	4.84	164.0	2.2148	7.20

TABLE 22

Equation of state : Ethyl glycol-water, 25°C

 $\alpha = 76$, dynes/cm/mol/l

Molarity c	Film pressure π dynes/cm.	$\log \pi$	$(\log \pi / \pi) 10^2$	$\pi' = \alpha c$	$\log \pi'$	$(\log \pi' / \pi) 10^2$
0.0605	3.90	0.5911	15.10	4.60	0.6628	17.00
0.0714	4.40	0.6435	14.60	5.43	0.7348	16.70
0.0988	5.30	0.7243	13.64	7.51	0.8756	16.50
0.1310	6.60	0.8195	12.40	9.96	0.9983	15.10
0.1580	8.20	0.9738	11.12	12.00	1.0792	13.10
0.190	9.10	0.9590	10.52	14.40	1.1584	12.70
0.218	10.65	1.0274	9.65	16.60	1.2201	11.50
0.298	11.90	1.0755	9.05	22.70	1.3560	11.40
0.351	13.45	1.1287	8.39	26.70	1.4265	10.60
0.403	14.35	1.1568	8.06	30.60	1.4857	10.35
0.482	15.20	1.1818	7.77	36.60	1.5575	10.20
0.610	16.80	1.2253	7.30	46.40	1.6665	9.90

Contd.....

Table 22 (Contd.)

Molarity c	Film pressure π dynes/cm.	$\log \pi$	$(\log \pi / \pi) 10^2$	$\pi' = \alpha c$	$\log \pi'$	$(\log \pi' / \pi) 10^2$
0.736	18.20	1.2601	6.92	55.9	1.7474	9.60
0.834	19.45	1.2889	6.62	63.4	1.8021	9.26
0.960	20.50	1.3118	6.54	73.0	1.8833	9.10
1.072	22.00	1.3424	6.10	81.5	1.9112	8.70
1.210	23.00	1.3617	5.90	92.0	1.9638	8.50
1.330	24.25	1.3845	5.71	101.1	2.0047	8.26
1.490	25.35	1.4090	5.54	113.2	2.0539	8.10
1.745	27.40	1.4378	5.25	132.6	2.1225	7.74
2.115	29.15	1.4646	5.02	160.7	2.2059	7.56

TABLE 23

Equation of state : n-propyl glycol-water, 25°C

 $\alpha = 214$, dynes/cm/mol/l

Molarity c	Film pressure π dynes/cm.	$\log \pi$	$(\log \pi / \pi) 10^2$	$\pi' = \alpha c$	$\log \pi'$	$(\log \pi' / \pi) 10^2$
0.0166	3.60	0.5563	15.45	3.54	0.5495	21.02
0.0166	3.80	0.5798	15.23	3.56	0.5495	14.80
0.0222	4.40	0.6435	14.60	4.98	0.6768	15.80
0.0249	4.95	0.6946	14.02	5.33	0.7267	14.70
0.0332	5.75	0.7597	13.02	7.11	0.8519	14.80
0.0387	7.15	0.8543	11.95	8.28	0.9180	16.00
0.0525	8.45	0.9269	10.95	11.45	1.0588	12.50
0.0662	9.65	0.9845	10.20	14.20	1.1523	11.92
0.0827	11.45	1.0588	9.25	17.70	1.2480	10.90
0.0990	12.90	1.1106	8.57	21.20	1.3260	9.66
0.1100	14.20	1.1523	8.11	23.55	1.3720	10.65
0.1375	15.40	1.1875	7.71	29.40	1.4680	9.53
0.1422	16.40	1.2148	7.40	30.40	1.4840	9.06

Contd....

Table 23 (Contd.)

Molarity c	Film pressure π dynes/cm.	$\log \pi$	$(\log \pi / \pi) 10^2$	$\pi' = \alpha c$	$\log \pi'$	$(\log \pi' / \pi) 10^2$
0.1865	19.60	1.2920	6.60	40.00	1.6020	8.17
0.2715	21.10	1.3240	6.28	58.10	1.7640	8.35
0.3240	22.30	1.3480	6.04	69.40	1.8410	8.25
0.3760	23.35	1.3680	5.86	80.50	1.9060	8.15
0.4030	24.45	1.3880	5.67	86.20	1.9360	7.91
0.4890	25.70	1.4100	5.49	104.80	2.0200	7.85
0.5310	26.70	1.4270	5.34	113.80	2.0560	7.70
0.6550	28.70	1.4580	5.08	140.10	2.1460	7.46
0.780	30.35	1.4820	4.88	167.00	2.2227	7.30
0.895	31.75	1.5020	4.74	192.00	2.2833	7.18
1.110	34.15	1.5330	4.49	238.00	2.3766	6.96

TABLE 24

Equation of state : n-butyl glycol-water, 25°C

 $\alpha = 625$, dynes/cm/mol/l

Molarity c	Film pressure π dynes/cm.	$\log \pi$	$(\log \pi / \pi) 10^2$	$\pi' = \alpha c$	$\log \pi'$	$(\log \pi' / \pi) 10^2$
0.010	5.90	0.7709	13.05	6.23	0.7945	13.45
0.013	7.05	0.8482	12.00	8.10	0.9085	12.90
0.014	7.95	0.9004	11.30	8.72	0.9405	11.82
0.019	9.50	0.9777	10.30	11.85	1.0738	11.30
0.024	10.75	1.0315	9.60	14.95	1.1747	10.95
0.029	11.95	1.0774	9.00	18.10	1.2577	10.52
0.034	13.15	1.1189	9.05	21.20	1.3263	10.10
0.040	14.25	1.1538	8.10	24.90	1.3962	10.15
0.051	15.35	1.1861	7.70	31.80	1.5024	9.80
0.061	16.35	1.2135	7.41	38.00	1.5998	9.65
0.069	18.20	1.2601	6.92	43.00	1.6335	8.97
0.078	19.48	1.2896	6.61	48.50	1.6857	8.65

Contd.....

Table 24 (contd.)

Molarity c	Film pressure π dynes/cm.	$\log \pi$	$(\log \pi / \pi) 10^2$	$\pi' = \alpha c$	$\log \pi'$	$(\log \pi' / \pi) 10^2$
0.0896	20.58	1.3135	6.40	55.7	1.7459	8.50
0.0985	21.68	1.3361	6.15	61.3	1.7875	8.25
0.1135	22.88	1.3594	5.94	70.7	1.8494	8.08
0.1245	23.68	1.3744	5.80	77.6	1.8890	7.96
0.1540	25.48	1.4062	5.51	96.0	1.9823	7.76
0.1798	26.88	1.4294	5.31	112.0	2.0492	7.63
0.2060	28.13	1.4492	5.15	128.2	2.1079	7.50
0.2580	30.23	1.4804	4.90	161.0	2.2068	7.31
0.3120	31.63	1.5001	4.74	194.5	2.2889	7.24
0.3640	32.88	1.5170	4.61	226.2	2.3545	7.15
0.4140	34.98	1.5438	4.42	258.0	2.4116	6.90
0.5400	36.93	1.5674	4.24	336.5	2.5269	6.83

CHAPTER 10

THE FREE ENERGY OF GLYCOL ETHER ADSORPTION AT
THE AIR-WATER INTERFACE

INTRODUCTION

Several authors have used the equation $\Delta G = -RT \ln \frac{C_s}{C_1}$ to obtain the free energy of adsorption (ΔG) of one component from a solution. C_s is its concentration in the surface layer and C_1 its concentration in the bulk phase. The values of C_s used in the above equation depend on the thickness assumed for the adsorbed layer and hence on the assumed orientation and configuration of the adsorbed molecules. Moreover, it is assumed that concentration may replace activities. This is probably a good approximation for many dilute solutions but may well be far from satisfactory for the adsorbed phase as experimental results tend to refer to high fractional coverages of the surface.

The need for introducing a thickness factor in C_s is overcome by an approximation suggested by Mankowich⁵⁵. He has expressed C_1 also in molecules/cm² of interface.

ΔG is a constant property of any given adsorbate so long as C_s is proportional to C_1 , which is the case in very dilute solutions only. Addison¹² determined the C_s-C_1

curve for each alcohol of the homologous series and obtained the value of C_s/C_1 from the slope of the tangent to this curve at the origin. Then ΔG was calculated from the Langmuir equation

$$G = -RT \log C_s / \tau C_1$$

assuming thickness of surface layer to be 6 \AA^2 .

The method of Ward and Tordai⁶⁵ was adopted by Posner, Anderson and Alexander¹⁴ and free energy of adsorption was calculated from the relation

$$\Delta G = -RT \ln \frac{\alpha}{\tau kT}$$

where concentrations were sufficiently low so that activity coefficients may be set equal to unity. α is the Traube coefficient in dynes/cm/molecule/c.c., τ is the thickness of surface region in cms.

RESULTS AND DISCUSSION

The ΔG values calculated using the above equation are recorded in Table 25. Comparison between polyoxymethylene and polymethylene chains may be made to show the difference produced when every third methylene group of the latter, in effect, is replaced by an oxygen atom. The value of ΔG , about 250 cal per $-\text{CH}_2\text{OCH}_2-$ is considerably less compared to $\Delta G = 650$ cal per $-\text{CH}_2-$, despite the fact that each

repeating unit contains three atoms in the straight chain instead of only one. The same increase in ΔG per $-\text{CH}_2-\text{OCH}_2$ was observed by Lovell and Hibbert⁸, based on surface tension of aqueous solutions of polyoxyethylene glycols. A comparison with corresponding alcohols, assuming ether-O- as equivalent to one CH_2 group in the chain reveals that ΔG values of the alcohols are considerably larger than those of the alkyl glycols. Similar comparisons of boiling points of methyl, ethyl and butyl glycols (124.5, 135, and 171) with those of n-butyl, n-amyl and n-hexyl alcohols (118, 138 and 175) were made by Scatchard and Wilson⁶⁶. Since the larger the value of ΔG , the greater the corresponding surface adsorption to occur, it follows that water has greater attraction for ether -O- than it has for $-\text{CH}_2-$; the alkyl glycols are less strongly adsorbed than the alcohols of similar chain length, because ether group is more polar than the $-\text{CH}_2-$ group.

The values of ΔG were substituted into the equation

$$\Delta G = \Delta G^{\circ} + kn$$

where n is the number of carbon atoms in the molecule and k is a constant. Langmuir found for several of series of compounds that ΔG° (a constant characteristic of $\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$ group) was reasonably same if $k = 625$, and this value has been

TABLE 26

Free energy - ΔG° compared with n-alcohols

	n-alcohol - $\Delta G^\circ, 20^\circ$ cals/g.mol	n-alkyl glycol - $\Delta G^\circ, 25^\circ$ cals/g.mol	Contribution due to -CH ₂ -O-CH ₂ - cals/g.mol
Methyl	1180	1455	275
Ethyl	1810	2090	280
n-propyl	2460	2700	240
n-butyl	3070	3300	230

TABLE 27

Free energy - ΔG° compared with n-alcohols taking
O = CH₂

	n-alcohol - $\Delta G^\circ, 20^\circ$ cals/g.mol	n-alkyl glycol - $\Delta G^\circ, 25^\circ$ cals/g.mol
n-butyl	2660	1455
n-amyl	3360	2090
n-heptyl	4050	2700
n-hexyl	4720	3300

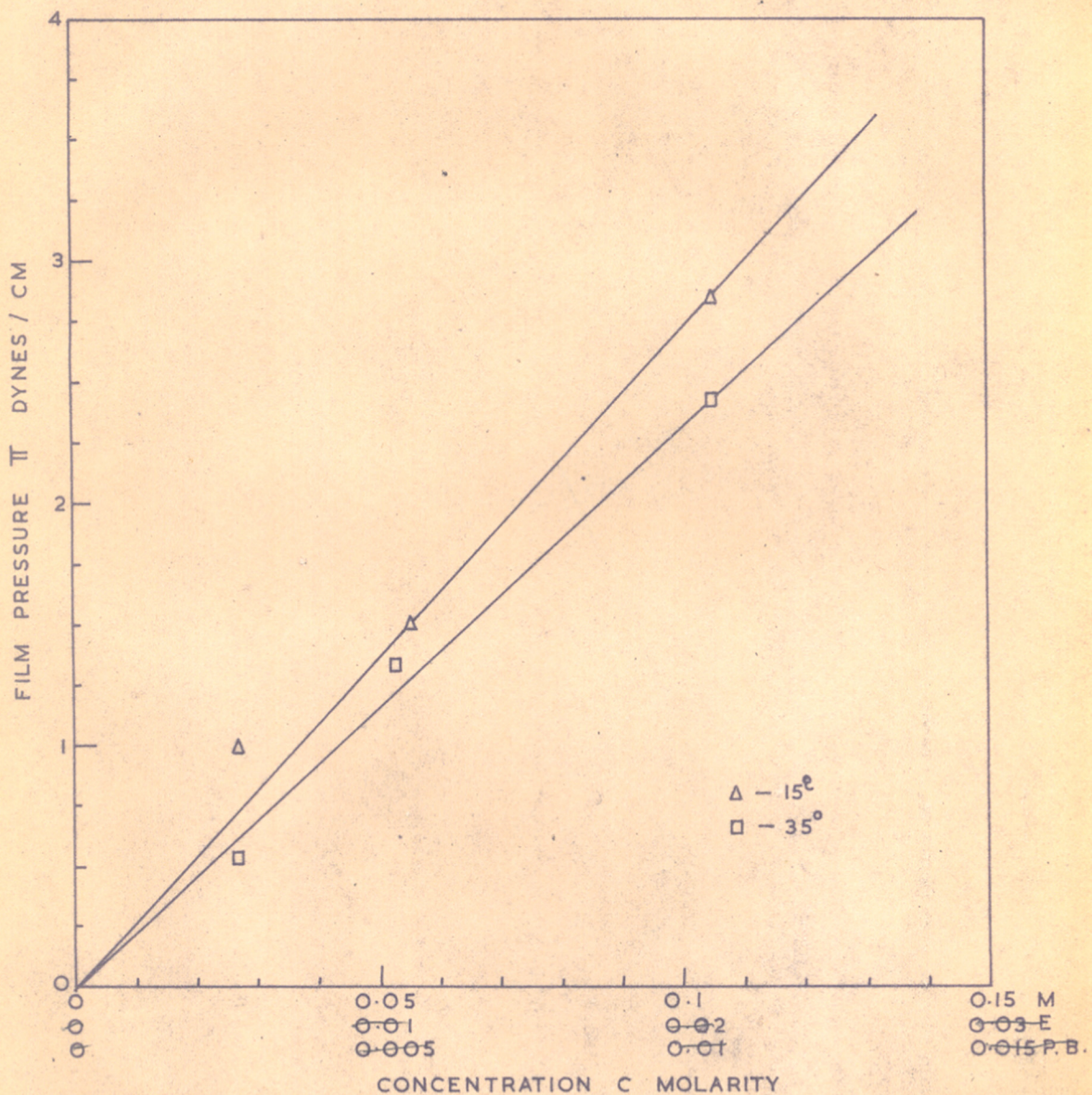
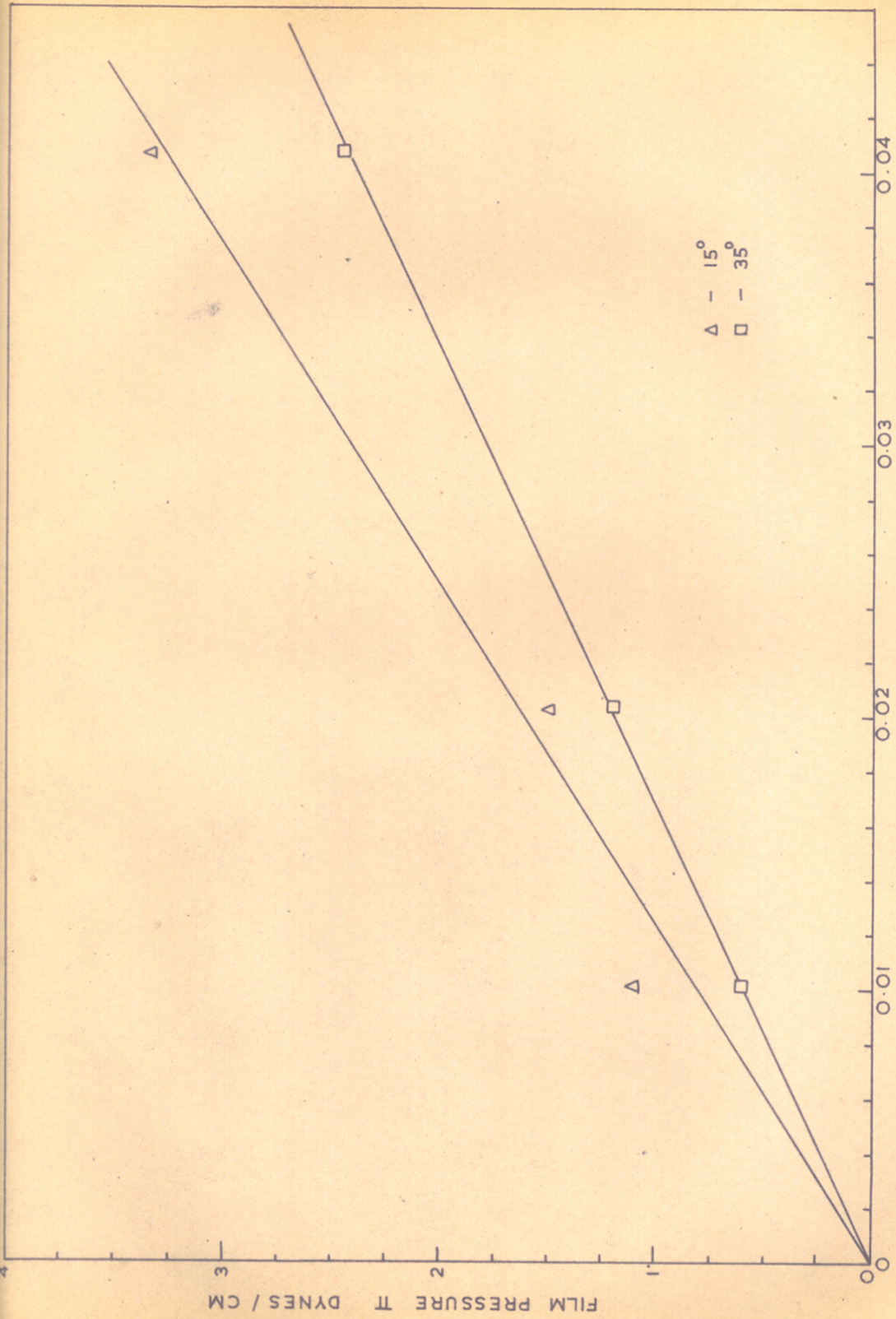


FIG. 9. FILM PRESSURE π VS. CONCENTRATION AT 15° AND 35°
METHYLGlyCOL-WATER SOLUTIONS



CONCENTRATION C Molarity
 FIG. 10. FILM PRESSURE π VS CONCENTRATIONS AT 15° AND 35°
 ETHYL GLYCOL - WATER SOLUTIONS

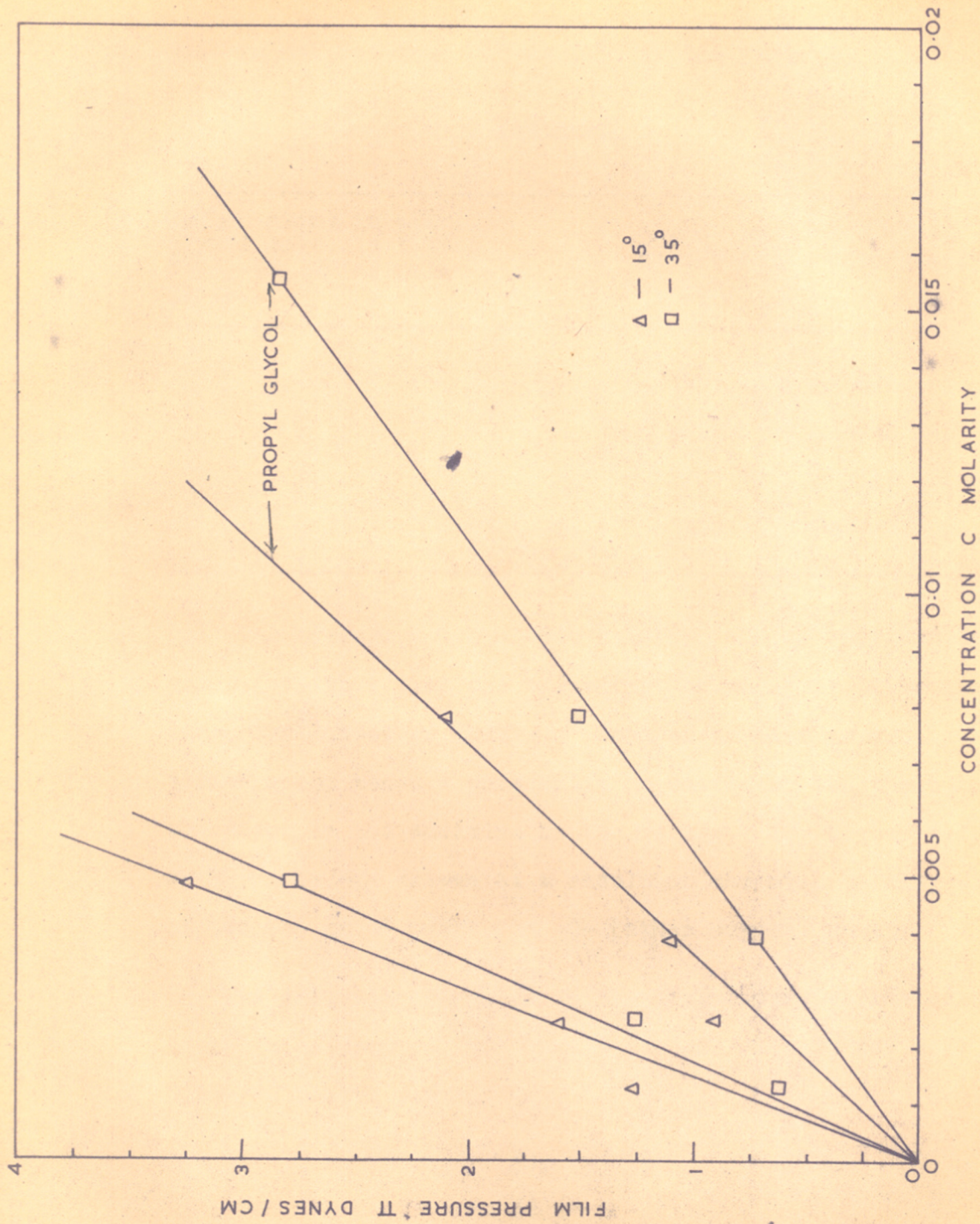


FIG. 11. FILM PRESSURE π VS CONCENTRATION AT 15° AND 35°

PROPYL GLYCOL - WATER SOLUTIONS AND BUTYL GLYCOL-WATER SOLUTIONS

used in determining ΔG° at 25°C in the Table H.

Table - H

Carbon atoms in alkyl glycol molecule taking $\text{O}-\text{CH}_2-\text{CH}_2.\text{OH}$ as polar group.	ΔG cals/g.mol 25°C	ΔG° cals/g.mol
1	1455	830
2	2090	840
3	2700	825
4	3300	800

The average value of 825 cal for ΔG° of $-\text{OCH}_2-\text{CH}_2.\text{OH}$ group is higher than the value for $-\text{OH}$ which is 575 cal. Langmuir³⁸ observed that ΔG° becomes smaller as the active group becomes more polar in character and the polar character is not additive in the series. The higher value of 825 cal has arisen as a result of the overwhelming effect of two CH_2 groups over the $-\text{O}-$ (ether oxygen) group.

As indicated in Table 25 the temperature variation of G is not considerable for calculation of H with the help of Gibbs-Helmholtz equation.

TABLE 25

Free energy of adsorption of alkyl glycols

	t °C	Traube's coefficient α (dynes/cm/mol/l)	α/kT	$\Delta G = 2.303 RT \log \alpha/kT$ cal/mole
Methyl glycol	15	27.3	12.68	1459
	25	26.0	12.10	1453
	35	23.8	10.31	1432
Ethyl glycol	15	80.5	37.25	2073
	25	76.0	34.55	2092
	35	59.0	25.61	1989
n-propyl glycol	15	268.0	121.0	2761
	25	214.0	96.0	2706
	35	182.0	79.0	2679
n-butyl glycol	15	656.0	304.2	3273
	25	623.0	279.5	3339
	35	565.0	245.9	3374

PART - II : VAPOUR LIQUID EQUILIBRIUM

CHAPTER 1

INTRODUCTION

In calculating surface excess at the liquid-vapour interface according to the accurate form of the Gibbs equation, activity data are also required in addition to surface tension. Activity a_1 is defined as the ratio of fugacities of components 'i', in any state compared to its fugacity in the standard state, thus

$$(a_1)_T = (f_1/f_1^0)_T \quad \dots (1)$$

If the vapour is assumed to behave ideally, partial pressures may be substituted for fugacities and the expression becomes

$$(a_1)_T = (p_1/P_1)_T \quad \dots (2)$$

where p_1 is the partial pressure of constituent 'i' and P_1 is the vapour pressure of pure liquid 'i' at the given temperature. In order to determine the partial vapour pressures for a mixture of two liquids, the method generally adopted is to measure the total pressure and composition of the vapour in equilibrium with a given liquid mixture at a definite temperature. If the liquid phase is ideal, Raoult's

law is applied. This law states that the partial pressure p_1 of any component in the vapour is equal to its mole fraction in the liquid x_1 times the vapour pressure P_1 of the pure component at the same temperature. Thus for the two components in a binary mixture

$$p_1 = P_1 x_1, \quad p_2 = P_2 x_2$$

If the gas phase is ideal, Dalton's law is followed. Accordingly the partial pressure p_1 of any component in the vapour is equal to its mole fraction in the vapour y_1 times the total pressure of the system P . Again for two components

$$p_1 = Py_1, \quad p_2 = Py_2$$

Therefore for each component 'i' in a binary mixture,

$$y_i P = p_i = x_i P_i$$

The above equations hold good for ideal solutions but most of the binary mixtures are nonideal in the liquid phase. Assuming that the vapour phase is ideal, deviations from ideality in the liquid phase are treated as multiplying factors. These are the activity coefficients. Activity coefficients γ are defined as the activities divided by their respective mole fractions or

$$\gamma_1 = a_1/x_1, \quad \gamma_2 = a_2/x_2$$

As according to equation (1)

$$a_1 = f_1/f_1^0$$

$$\gamma_1 = f_1/f_1^0 x_1$$

According to equation (2), where the vapours are perfect gases

$$f_1 = p_1 \text{ and } f_1^0 = P_1, \text{ so that}$$

$$\gamma_1 = \frac{p_1}{P_1 x_1} = \frac{p y_1}{P_1 x_1}$$

$$\gamma_2 = \frac{p_2}{P_2 x_2} = \frac{p y_2}{P_2 x_2}$$

If the vapours do not behave as ideal gases, however, the nonideality of the vapour phase has to be accounted for. This is done by replacing $y_1 P$ in the above equations by $\theta y_1 P$ where

$$-\ln \theta_1 = \frac{(V_1 - \beta_1) (P - p_1)}{RT}$$

In the latter V_1 is the liquid molal volume of 'i' and β_1 is the vapour compressibility factor of 'i'. The factor β_1 may be evaluated from generalized equation of state with sufficient accuracy.

$RT \ln \gamma_1$ represents the free energy change involved in transferring a mole of component 'i' from an environment

of 'i' molecules into the solution environment in question which is in excess of that which would be involved if the solution were perfect.

In dealing with vapour-liquid equilibria, it is convenient to interpolate or extrapolate with use of analytical relations between activity coefficients and concentrations. Even though these are derived by differentiating some expression for the excess free energy of solution, they may be viewed simply as empirical relations, used to constant temperature. One of the widely used two parameter equation of binary mixtures is that of van Laar,

$$\log \gamma_1 = \frac{A_{12}}{\left(1 + \frac{x_1 A_{12}}{x_2 A_{21}}\right)^2}$$

$$\log \gamma_2 = \frac{A_{21}}{\left(1 + \frac{x_2 A_{21}}{x_1 A_{12}}\right)^2}$$

where the parameters are A_{12} and A_{21} . These can be considered as the logarithms of the two limiting activity coefficients. The limiting activity coefficients provide the two parameters for interpolation from infinite dilution to finite concentration. This equation, however, is incapable of fitting system which has a maximum in the $\log \gamma$ vs. x curve. Margules which is another equation for binary mixtures is suitable for systems with maxima in $\log \gamma$ vs. x curves, but van Laar gives a better fit to unsymmetrical systems than Margules.

The determination of the constants of the van Laar

equation for the systems methyl glycol-water and ethyl glycol-water under isothermal conditions is described in the following pages. The most precise method of determining these is to calculate the constants from known equilibrium compositions of the vapour and liquid. Theoretically one experimental point is adequate for calculation of A and B,

$$A = \log \gamma_1 \left(1 + \frac{x_2 \log \gamma_2}{x_1 \log \gamma_1} \right)^2$$

$$B = \log \gamma_2 \left(1 + \frac{x_1 \log \gamma_1}{x_2 \log \gamma_2} \right)^2 .$$

Usually however several equilibrium compositions are determined. For each of them, we then calculate the corresponding constants A and B and take their averages.

Before our work started on alkyl glycols Baker and Hubbard⁵⁶ had studied two-phase equilibrium of ethyl glycol-water isobarically at 760 mm and from x-y data showed that the system had a constant boiling mixture with 92.1 mole percent water.

Newman, Hayworth and Treybal⁵⁷ determined vapour-liquid equilibrium of n-butyl glycol-water in an Othmer type still at 760 mm. The activity coefficients were calculated from equilibrium data and correlated. The results were utilized alongwith methyl ethyl ketone-water results to get ternary equilibrium data.

Boublik and Kuchynka³⁵ investigated the vapour liquid equilibrium of ethyl glycol-water system at different pressures. The results of measurement were correlated with van Laar's equation.

Jakubicek, Fried and Vahála³⁴ determined equilibrium data in the binary system water-methyl glycol at 100 mm.Hg. and 752 mm.Hg. The van Laar constants were $A = 0.054$ and $B = 0.264$ and $A = 0.302$ and $B = 0.592$ at 100 mm and 752 mm, respectively.

Schneider and Wilhelm⁵⁸ studied the system butyl glycol-water at higher temperatures and pressures, where no phase separation occurs throughout the concentration range. The results were useful in calculating the excess free energy of mixing.

No work is reported on the isothermal vapour liquid equilibrium measurements on methyl glycol-water and ethyl glycol-water systems. This work was originally started with the intention of getting the temperature relation of van Laar constants of the above systems and utilise it for calculating the activities.

CHAPTER 2

GENERAL METHODS

The direct experimental determination of vapour-liquid equilibrium means that we separate samples of the liquid and vapour which are in true equilibrium and determine concentrations of both phases analytically. The generally used methods are :

- 1) Distillation method
- 2) Static method
- 3) Dew and bubble point method
- 4) Flow method
- 5) Circulation method

In the distillation method a small amount of the liquid is distilled off from a large charge. The draw-backs in this method are difficulty in maintaining the composition of the liquid phase constant while distilling off vapour sample and condensation on the cold walls of the apparatus.

The static method involves equilibrating liquid and vapour phase in a thermostated vessel and withdrawing samples of the phases for analysis when equilibrium has been established. At low pressures the amount of the vapour phase

required is of the same order as the total amount of vapour, so that removal of a sample causes marked disturbance of the equilibrium.

In the dew and bubble point method, the pressure at which a mixture of known composition just begins to vapourise or to condense is measured to determine equilibria.

In the flow method, in distinct contrast to the circulation one, we feed to the equilibrium chamber, a steady stream of constant composition which can be either in the liquid or in the vapour phase or a combination of the two.

The most commonly used is the circulation technique which involves continuous single theoretical plate distillation. In the recirculating still both the liquid and vapour phases are recirculated at whatever rate they happen to be generated until a steady state is reached. Samples are then withdrawn for analysis.

The recirculation type of stills cannot be conveniently used at pressures lower than 50 mm. Charges to the still may vary between 50-500 ml. The time taken to achieve a steady state is usually moderate.

A good still consists of (1) a boiler for generating vapour, which also holds the major portion of the charge (2) a space for disengaging liquid and vapour, (3) a means

of condensing the vapour stream, with a hold up to supply a sample for analysis, (4) a means of returning the condensed vapour to the reboiler, (5) arrangement for measuring temperature, (6) a means of regulating pressure and measuring for isothermal work, (7) a means of withdrawing liquid and condensed vapour samples for analysis.

The operation of the still consists of (1) the pressure and temperature at some level, (2) boiling the charge at some constant rate until the condensed vapour has been recirculated a number of times, and both compositions and temperature have arrived at a steady state, (3) withdrawing samples with a minimum disturbance of the system, (4) analysing the samples.

Careful attention has to be given to the following :

(1) loss of heat from the disengaging chamber must be minimum since any condensation here will remove heavier components from the vapour stream. Transfer of heat into the disengaging chamber must be a minimum since evaporation of liquid spray from parts superheated with respect to the measured equilibrium temperature will tend to give an unrepresentative vapour sample. The disengaging chamber of the still must be insulated from the surroundings and supplied with a heater outside the insulation. (2) The disengaging chamber must be designed in such a way that the carrying over

of liquid droplets into vapour line is avoided. (3) There should not be any channeling through some portion of the reboiler while recirculating the condensed vapour.

This type of recirculating stills can be used for constant temperature measurement by adjusting the pressure for each experimental point until steady predetermined, temperature is attained. The γ 's are not very sensitive to temperature but, ^{temperature} must be accurately known for calculation purposes. The points obtained are described in terms of composition, temperature, and total pressure (x , y , t , p). These overspecify the system but measurement of temperature and pressure provide convenient internal check on each point.

The vapour-liquid equilibrium measurement by the recirculation technique is described in Chapter 4.

CHAPTER 3

VAPOUR PRESSURES OF PURE COMPONENTS

For the characterisation of vapour-liquid equilibrium it is necessary to measure the pressure of the saturated vapours of the pure components at different temperatures. There are two possible ways of determining this :

- a) Dynamic method
- b) Static method.

When using the dynamic method we measure the temperature at which the liquid and vapour phases are in equilibrium under constant pressure. On the other hand, the static method involves the measurement of the pressure of vapours which are established over the liquid at constant temperature.

DYNAMIC METHOD (Measurement of Boiling Point)

The older method of using a vessel containing a boiling liquid into which a thermometer is immersed, is erroneous, the boiling liquid is always superheated since the surface tension of the liquid prevents evolution of small bubbles of vapour. It is thus necessary have a higher pressure of the vapours to overcome it. Also the

hydrostatic pressure of the liquid superheats the liquid at the bottom of the vessel.

By placing the thermometer in the vapour space above, the condensation temperature is measured and this is identical with the boiling point only with extremely pure substances. To avoid the above difficulties ebulliometers are used to measure boiling points accurately.

The ebulliometer with Cottrel pump device functions as follows : A mixture of liquid and vapour is pumped through a small tube which ends in a funnel, by heating the liquid to boiling. The evolved vapours rise through the tube and continuously carry with them slugs of liquid. The liquid spurts onto a thermometer pocket. Equilibrium between the liquid and vapour phases is first established on this thermometer pocket. In this investigation the boiling points were measured at different pressures in the equilibrium still described in Chapter 4, which functioned as an ebulliometer.

(a) The methyl glycol, ethyl glycol and water were purified and tested as indicated in Part I of this thesis.

(b) A rod type of mercury thermometer (range 0-110°C) subdivided in 0.1°C) was used for the measurement of temperature. Correction was applied for the mercury thread exposed above the thermometer well. This correction was

read off directly from the table given in Ref.59, p. 161.

(c) A U-tube type open mercury manometer was made use of for pressure measurement in conjunction with a precise barometer. The pressures measured with a cathetometer were corrected to 0°C and recalculated to the standard value of gravity g^0 (980.665 cm/sec²) by means of the equation

$$h_s = h_0^0 g/g^0$$

h_s is the corrected value of h_0^0 . h_0^0 is the observed mercury column height and $g = 978.4$ cm/sec². The temperature correction was read off from nomogram given in Ref.60, p.183. The results are indicated in Tables 28 to 30.

The accuracy of measuring temperature and pressure were tested by measuring the boiling points of water in the still. The vapour pressure data are in good agreement with the already published data as seen in Table 28.

The thermodynamic expression of phase equilibrium for a pure substance is given by the Clapeyron equation

$$\frac{dp^0}{dT} = \frac{\Delta H_{\text{evap.}}}{T \Delta V}$$

On introducing the compressibility factor this equation takes the form

$$\frac{d \ln p^0}{d (1/T)} = \frac{\Delta H_{\text{evap.}}}{R \Delta z}$$

where $\Delta z = z'' z'$, the symbols z'' and z' denote the

compressibility factors of the vapour and liquid phases respectively. This equation is more precise than the Clausius Clapeyron equation since the factor Δz includes both the correction for nonideality of the vapour phase and that for the volume of the liquid phase.

The simplest semi-empirical equation for the dependence of the vapour pressure on temperature is obtained by integrating the equation above under the simplifying assumption that

$$\frac{\Delta H_{\text{evap.}}}{\Delta z} = \text{const.}$$

which gives

$$\log P^{\circ} = A - B/T$$

But the dependence of $\log P^{\circ} = f(1/T)$ is linear only in a narrow range of temperatures. A whole series of equations has therefore been proposed, various authors having modified the right side of the equation in different ways.

The Antoine equation has the form

$$\log P^{\circ} = A - B/(t+C)$$

where A, B and C are constants.

A further simplification of the Antoine equation is the modification proposed by Calingaert and Davies⁶¹,

who evaluated the average value of the constant C in Antoine equation. The equation has the form

$$\log P^{\circ} = A - B/(t + 230)$$

Tables 29 and 30 show the vapour pressures of purified methyl and ethyl glycols at different temperatures upto the boiling point. The temperature dependence is expressible by the equations⁶²

$$\log P^{\circ} = 7.7085 - 1711.2/(t+230)$$

and

$$\log P^{\circ} = 7.8191 - 1801.9/(t+230)$$

for methyl and ethyl glycol respectively. The experimental values deviate from the calculated values maximum to the extent of 2%.

TABLE 28

Vapour pressure of water

Boiling point $t^{\circ}\text{C}$	Pressure P mm.Hg. observed	P literature value
54.7	111.9	116.5
59.8	144.5	148.0
64.7	181.5	184.5
69.9	227.6	232.7
75.1	286.2	290.3
80.4	353.6	360.5
85.2	431.7	437.0
90.3	527.5	531.8
95.9	651.6	653.8

TABLE 29

Vapour pressure of methyl glycol

Boiling point t°C	Pressure P mm.Hg. observed.	P calculated according to empirical equation
65.7	84.84	83.3
77.9	137.00	141.3
93.6	265.95	263.3
102.9	372.4	369.4
110.9	486.1	487.7
115.0	562.0	559.5
122.0	704.5	703.4

$$\log P = 7.7085 - 1711.2/t + 230$$

TABLE 30

Vapour pressure of ethyl glycol

Boiling point $t^{\circ}\text{C}$	Pressure P mm.Hg. observed	P calculated according to empirical equation
79.95	100.01	101.3
85.90	128.30	130.3
91.10	160.20	161.3
95.85	192.40	194.6
100.65	239.40	234.3
106.30	289.24	289.20
110.50	336.40	336.7
115.40	399.00	399.9
120.60	479.1	478.3
125.90	573.3	569.6
129.90	651.7	649.4
132.50	707.1	705.3

$$\log P = 7.8191 - 1801.9/t + 230$$

CHAPTER

EXPERIMENTAL DETERMINATION OF ACTIVITY
COEFFICIENTS FROM EQUILIBRIUM MEASUREMENTS

The apparatus used in this study is of the conventional recirculating type made of pyrex glass and is a modification of the Gillespie type still⁶³. In the Fig.12 the complete assembly with accessories is illustrated. The liquid mixtures are electrically heated in the boiling chamber B⁶⁴. The external heater is made of winding nichrome wire on a silica tube. The internal heater is made from 40 cms of 28 SWG platinum wire and is wound round the inner side of the annular space. The heated charge is forced up the tube P alongwith its vapours and splashes on to the thermometer well W. The two phase separate in the chamber O, the vapour condenses in the chilled water condenser C. The condensed vapour overflows from the trap T_c and is recirculated through trap T₁. The charge of the still is 125 cm³, distributed as follows : 5 cm³ in vapour trap, 10 cm³ in liquid trap and 110 cm³ in boiler.

Temperature is measured to 0.1° with a calibrated mercury in glass thermometer in the well W. Exposed stem

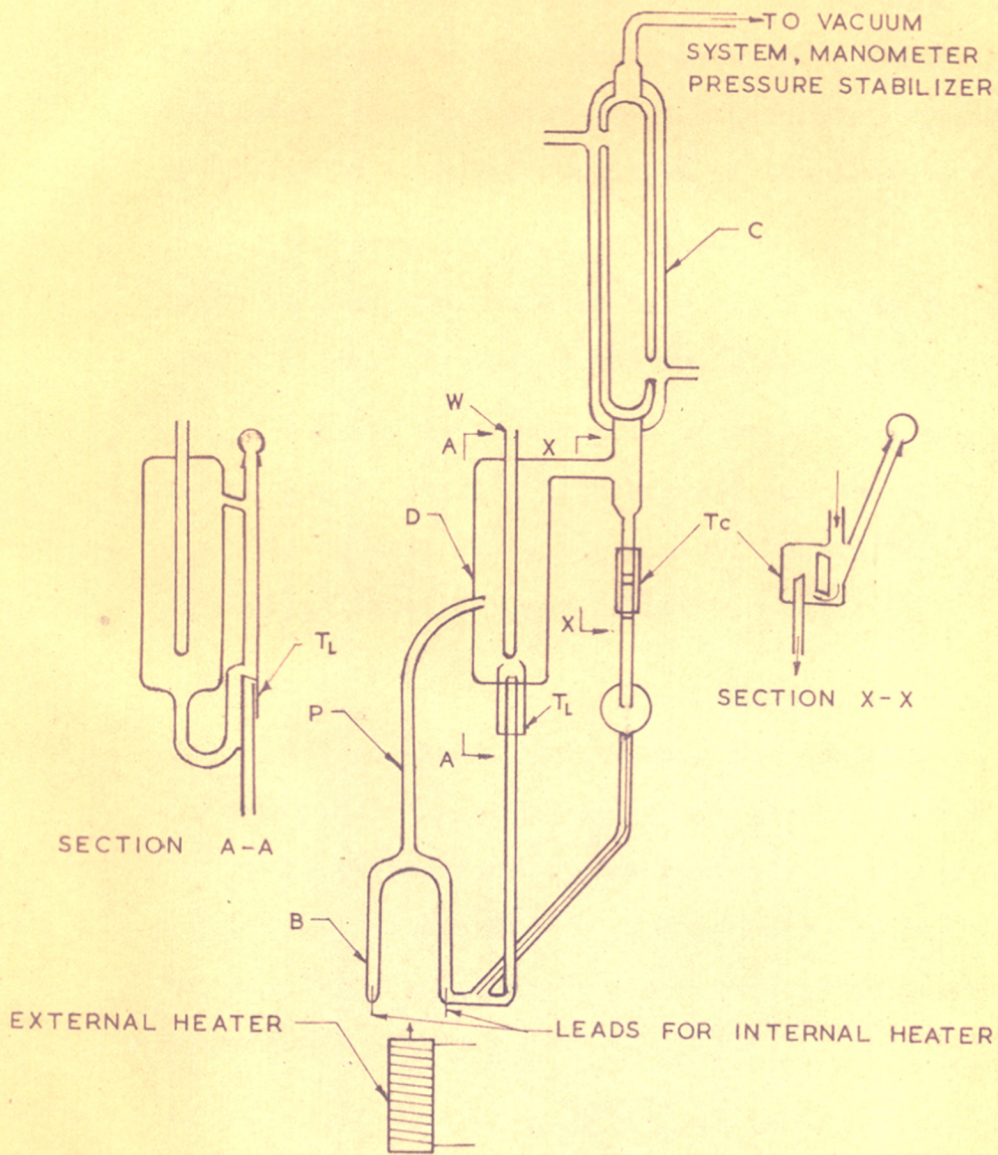


FIG. 12. THE EQUILIBRIUM STILL

corrections are applied.

Pressure is measured to 0.1 mm.Hg. with an open mercury manometer and cathetometer in conjunction with a barometer. The cathetometer and barometer readings are corrected to standard condition of temperature and gravity.

The pressure is stabilised by two 10 L round bottomed pyrex flasks, thermostated to $\pm 0.1^{\circ}\text{C}$. The connection from the still to vacuum system is made at M.

Boiling is interrupted after about 4 hrs., samples in the traps are chilled with cracked ice and then syphoned out into chilled stoppered conical flasks for analysis by refractive index or density measurements.

RESULTS

Tables 31, 32 and 35 gave the measured equilibrium data for methyl glycol-water and ethyl glycol water systems. The small corrections to the activity coefficients arising out of the nonideality in vapour phase are neglected. The values of constants A and B calculated according to equations

$$A = \log \gamma_1 \left(1 + \frac{x_2 \log \gamma_2}{x_1 \log \gamma_1} \right)^2$$

$$B = \log \gamma_2 \left(1 + \frac{x_1 \log \gamma_1}{x_2 \log \gamma_2} \right)^2$$

as shown in Tables 33, 34 and 36.

DISCUSSION

The average values of A and B of ethyl glycol-water system at 90° are in good agreement of values obtained by Boublik and Kuchinka³⁵ by isobaric measurements at 400 mm., temperature range $82-87^{\circ}\text{C}$.

<u>Present values</u> <u>Isothermal at 90°</u>	<u>Isobaric values at 400 mm.</u> <u>B.P.'s between $82-87^{\circ}\text{C}$.</u>
A 0.238	0.28
B 0.785	0.77

A few measurements are also made at 65°C for the system methyl glycol water. The constants are not in very good agreement with isobaric literature values. As the temperature coefficient of A and B is not considerable to be estimated accurately by this still further experiments were not conducted.

The design and construction of the equilibrium still can be a source of various errors. The errors are dependent on relative volatility, latent heats of vapouration etc., of the system. So far it has not been possible to construct a still which would yield consistent data for all systems.

The present still and method of analysing vapour and liquid composition (Abbe's refractometer with accuracy of 5

in the fourth place of decimal) are not capable of giving accurate data beyond about 0.7 mole fraction of solute.

The van Laar equation can be transformed to the form

$$(\log \gamma_1)^{-0.5} = \frac{A^{0.5}}{B} \frac{x_1}{x_2} + \frac{1}{A^{0.5}}$$

$$(\log \gamma_2)^{-0.5} = \frac{B^{0.5}}{A} \frac{x_2}{x_1} + \frac{1}{B^{0.5}}$$

From these equations, it is seen if we plot $(\log \gamma_1)^{-0.5}$ vs. x_1/x_2 and $(\log \gamma_2)^{-0.5}$ vs. x_2/x_1 , we should obtain straight lines, whose intercepts on the ordinate axis give the reciprocal values of roots of A and B. But such a long extrapolation is sensitive to small errors in the data points and so not attempted. It is clearly essential to carry out further work by redesigning the still and also improving the precision of the analytical data.

TABLE 31

Uncorrected activity coefficients : Methyl glycol water
 Temperature 90° ; P_1 = vapour pressure of water 522.0 mm.Hg.
 P_2 = vapour pressure of methyl glycol 229.9 mm.Hg.

x_{H_2O}	y_{H_2O}	P pressure in mm.Hg.	γ_1 (uncor)	γ_2 (uncor)
0.927	0.938	531.5	1.001	1.912
0.913	0.932	532.3	1.012	1.762
0.888	0.914	530.0	1.015	1.729
0.871	0.905	526.6	1.018	1.660
0.842	0.888	524.8	1.030	1.585
0.818	0.877	522.0	1.043	1.491
0.784	0.868	520.4	1.072	1.355
0.764	0.855	516.4	1.075	1.352
0.750	0.848	509.9	1.073	1.311
0.702	0.824	499.5	1.089	1.255

TABLE 32

Uncorrected activity coefficients : Ethyl glycol-water

Temperature 90° ; P₁ = vapour pressure of water 522.0 mm.Hg.P₂ = vapour pressure of ethyl glycol 154.5

x H ₂ O	y H ₂ O	P Pressure in mm.Hg.	Y ₁ (uncor)	Y ₂ (uncor)
0.858	0.907	535.0	1.078	2.250
0.901	0.920	535.8	1.043	2.785
0.884	0.913	532.6	1.048	2.580
0.837	0.900	526.6	1.079	2.093
0.807	0.898	522.0	1.106	1.787
0.786	0.893	521.0	1.126	1.698
0.793	0.896	518.3	1.115	1.691
0.728	0.882	511.1	1.181	1.428
0.768	0.878	504.5	1.177	1.406
0.682	0.874	497.2	1.215	1.270
0.633	0.849	471.2	1.205	1.250

TABLE 33

Constants of the van Laar equation from several direct determinations of the equilibrium vapour-liquid composition
Methyl glycol-water 90°

Mole fraction water x_1	A	B
0.927	0.180	0.405
0.913	0.162	0.354
0.888	0.216	0.341
0.871	0.200	0.371
0.842	0.197	0.392
0.818	0.184	0.391
0.784	0.145	0.428
0.764	0.170	0.425
0.750	0.164	0.382
0.702	0.163	0.357
	Mean 0.178	Mean 0.385

TABLE 34

Constants of the van Laar equation from several direct determinations of the equilibrium vapour-liquid composition Ethyl glycol-water 90°

Mole fraction water x_1	A	B
0.858	0.252	0.860
0.901	0.246	0.840
0.884	0.266	0.785
0.837	0.276	0.750
0.807	0.246	0.736
0.786	0.252	0.766
0.793	0.229	0.765
0.728	0.234	0.783
0.768	0.178	1.070
0.682	0.209	0.784
0.633	0.233	0.570
Mean	0.238	Mean 0.785

TABLE 35

Uncorrected activity coefficients : Methyl glycol-water

Temperature 65° ; P_1 = vapour pressure of water 187.5 mm.Hg.

P_2 = vapour pressure of methyl glycol 81.0 mm.Hg.

x_{H_2O}	y_{H_2O}	P Pressure in mm.Hg.	γ_1 (uncor)	γ_2 (uncor)
0.882	0.921	183.6	1.022	1.515
0.550	0.903	181.5	1.028	1.415
0.772	0.864	176.8	1.055	1.300
0.698	0.826	172.3	1.087	1.225
0.635	0.794	167.6	1.118	1.170

TABLE 36

Constants of the van Laar equation from several direct determinations of the equilibrium vapour-liquid composition
Methyl glycol-water 65°

Mole fraction water x_1	A	B
0.882	0.119	0.350
0.850	0.128	0.315
0.772	0.139	0.328
0.698	0.152	0.336
0.635	0.160	0.338
Mean	0.140	Mean 0.333

S U M M A R Y

Studies on the surface properties of alkyl glycol and polyoxyethylene glycol type of compounds are of considerable interest for the elucidation of their water evaporation retardation properties as insoluble monolayers and also for their detergency and dispersing ability. A systematic study of the surface chemical properties of simple alkyl glycols have been undertaken, so that they may serve as models helpful to a better understanding of the more complex molecules.

Surface tensions of pure liquids and aqueous solutions of the first four members in the homologous series of n-alkyl glycols (methyl, ethyl, propyl and butyl) have been measured as a function of temperature.

The temperature coefficient of surface tension of the pure liquids decreases, while that of latent heat of surface formation increases at almost the same rate. The enthalpy of surface formation, like most pure liquids, is practically independent of temperature. There is a decreasing tendency in the entropy of surface formation with increasing molecular weight. This seems to indicate that the degree of order in the liquid surface region increases with increase in chain length.

The Eötvös constant 'k' varies between 1.4 to 1.6

whereas for n-alcohols the variation reported in the literature is between 0.95 to 1.5.

The experimental parachor values agree with the calculated ones.

The activity coefficients of the solutes required for calculation of surface excess in aqueous solution have been obtained with the help of van Laar equation. The constants of the equation have been calculated for all the binary systems, by the method of Hala, Pick, Fried and Vilm. The literature data obtained by using different techniques where available, are found to be in agreement with our values.

It has been shown that the Traube's rule viz., $\alpha_n/\alpha_{(n-1)} \approx 3$ (where α is the limiting slope at the origin of the film pressure vs. concentration curve and n is the number of carbon atoms in the hydrophobic chain) is almost quantitatively valid for these systems.

The thickness of the adsorbed layer of methyl and ethyl glycols has been shown to be of the order of one molecule by applying the test proposed by Schay and Nagy to the adsorption isotherms.

The composite isotherms have been resolved into the individual isotherms. The composition of the adsorbed layers of methyl and ethyl glycols resemble those of the corresponding alcohols, but the propyl and butyl derivatives do not, perhaps due to their micellization in the media.

The cohesive force between these molecules in the monolayer are almost equivalent to that of n-alcohols with same chain length taking ether oxygen equivalent to one carbon atom. But the coarea per molecule obtained from the equation of state appears to be higher than the n-alcohols, probably due to hydrocarbon chains lying in a zigzag form on the water surface.

The free energy of adsorption of ethylene oxide group $-O-CH_2-CH_2$ group is only 250 cal/mole, compared to 620 cal/mole for a $-CH_2-$ group. The free energy of adsorption of the polar group $O-CH_2-CH_2-OH$ is 825 cal/mole, whereas that of alcohol OH is 590 cal/mole. The increase is due to the resultant of contributions to the free energy of adsorption by the polar groups and two CH_2 groups. The alkyl glycols are less surface active than the corresponding alcohols if $-O-$ group is considered as equal to $-CH_2-$ group.

The vapour pressures measured in the equilibrium still are in good agreement with literature values for methyl and ethyl glycols.

The vapour-liquid equilibrium measurements of the above glycol-water systems measured isothermally in a modified Gillespie still, yield van Laar constants, which are in good agreement with the isobaric values reported in the literature in the case of ethyl-glycol water systems.

REFERENCES

1. A.V. Deo, Ph.D. thesis, Poona University, 1962.
2. J.W. Gibbs, The collected works of Willard Gibbs, Longmans, Green and Co., New York, 1931, Vol.1 p.219.
3. E.A. Guggenheim and N.K. Adam, Proc.Roy.Soc. (London), A139, 218 (1933)
4. J.J. Kipling, Adsorption from solutions of non-electrolytes, Academic Press, New York, 1965.
5. K. Shinoda, T. Yamanaka, and K. Kinoshita, J.Phys.Chem. 63, 648 (1959).
6. J.M. Corkill, J.F. Goodman and R.H. Ottewill, Trans. Faraday Soc., 57, 1627 (1961).
7. M.J. Schick, J. Colloid.Sci., 17, 801 (1962).
8. E.L. Lovell and H. Hibbert, J.Am.Chem.Soc., 62, 2144, 1940.
9. A. Couper and D.D. Eley, J.Poly.Sci., 3, 345 (1948).
10. I. Traube, Annalen, 265, 27-55 (1891).
11. V. Szyskowski, Z. Phys. Chem., 64, 385 (1908).
12. C.C. Addison, J.Chem.Soc., (1945) 98.
13. C.C. Addison and S.K. Hutchinson, J.Chem.Soc. (1949) 3387, 3395.
14. A.M. Posner, J.R. Anderson and A.E. Alexander, J.Colloid. Sci. Z, 623 (1952).

15. H.H. King and R.W. Wampler, J. Am. Chem. Soc., 44, 1894 (1922).
16. L.H. Cretcher and W.H. Pittinger, J. Am. Chem. Soc., 46 1503 (1924).
17. Palomaa, Chem. Berichte, 35, 3350 (1902)
18. N.K. Adam, The physics and Chemistry of surfaces 3rd ed., Clarendon Press, Oxford, 1941.
19. J.J. Bikerman, Surface chemistry for Industrial Research, p.4, Academic Press, New York, 1947.
20. W.D. Harkins, and H.F. Jordan, J. Am. Chem. Soc., 52, 1751 (1930).
21. J.R. Hommelen, J. Colloid. Sci. 14, 385 (1959).
22. A. J. Vogel, J. Chem. Soc., (1948) 1818.
23. Moll, Koll. Beih, 49, 5 (1939) through Beilstein.
24. K. Yu. Chu and A.R. Thompson, J. Chem. Eng. Data., 5, 147 (1960).
25. R.C. Tallman, J. Am. Chem. Soc. 56, 127 (1934).
26. W. Ramsey and J. Shields, J. Chem. Soc. (1893) 1089.
27. O.A. Hougen, K.M. Watson and R.A. Ragatz, Chemical Process Principles, Asia Publishing House 1962, vol.1 p.88.
28. O. Exner, Collection Czech. Chem. Commun., 30, 24 (1967).
29. E. Hala, V. Fried, J. Pick and O. Vilim, Collection Czech. Chem. Commun. 21, 1381 (1956).
30. E. Erdős, Collection Czech. Chem. Commun., 21, 1528 (1956).

31. U. Onken, Z. Elektrochem. 63, 321 (1959).
32. Laar J.J. Van, Z. Physik, Chem. 72, 723-51 (1910);
83, 599-608 (1913).
33. H.C. Carlson and A.P. Colburn, Ind.Eng.Chem. 34,
581 (1942).
34. J. Jakubicek, V. Fried and J. Vahala, Chem.listy.,
51, 1422 (1957).
35. J. Boublik and K. Kuchynka, Collection Czech.Chem.
Commun., 21, 1634 (1956).
36. H.L. Cox and L.H. Cretcher, J.Am.Chem.Soc. 48, 451
(1926).
37. G.W. Wilson and CH. Deal, Ind.Eng.Chem. Fundamentals,
1, 20 (1962).
38. I. Langmuir, J.Am.Chem.Soc. 39, 1848, (1917).
39. A.F.H. Ward, Trans. Faraday Soc., 42, 399 (1946).
40. R.H. Aranow and L. Witten, J.Chem.Phys. 28, 405 (1958).
41. M.A. Higgs, J.Chem.Phys. 35, 1504, (1961).
42. R.H. Aranow and L. Witten, J. Chem. Phys. 35,
1504 (1961).
43. Lange Koll. Z. 163, 9, (1959).
44. G. Schay, L. Gy. Nagy and T. Szekrenyesy,
Periodica Polytechnica 4, 95, (1960).
45. G. Schay and L. Gy. Nagy, J.Chim.Physique, 149 (1961)
46. D.H. Haydon and F.H. Taylor, Phil.Trans., 252,
225 (1960).
47. W.D. Harkins and R.W. Wampler, J.Am.Chem.Soc., 53
850 (1931).

48. J.A.V. Butler, Proc. Roy. Soc. (London), A135, 348 (1932).
49. A.V. Deo, S.B. Kulkarni, M.K. Gharpurey and A.B. Biswas, Ind. J. Chem., 2, 43 (1964).
50. J.J. Kipling, J. Colloid. Sci., 18, 502 (1963).
51. F.M. Fowkes, J. Phy. Chem. 66, 385 (1962).
52. J.T. Davies, Trans. Faraday. Soc., 48, 1052 (1952).
53. R.K. Schofield and E.K. Rideal, Proc. Roy. Soc. (London) A 109, 57 (1925).
54. A.E. Alexander and A.M. Posner, Nature, 166, 1932 (1950).
55. M. Mankowich, J.A.O.C.S., 43, 615 (1966).
56. E.M. Baker and R.O.H. Hubbard, Ind.Eng.Chem. 31, 1260 (1939).
57. M. Newman, C.B. Hayworth and R.F. Treybal, Ind.Eng. Chem. 41, 2039 (1949).
58. G. Schneider and G. Wilhelm, Z.Physik.Chem. N.F. 20, 219 (1959).
59. Vapour liquid equilibrium. E. Hala, J. Pick, V. Fried, O. Vilim, Translated by G. Standart, Pergamon Press (1958), p.160.
60. E. Halá, J. Pick, V. Fried and O. Vilim, loc.cit., p. 183.
61. G. Calingaert and D.S. Davis, Ind.Eng.Chem., 17, 1287 (1925).
62. J. Pick, V. Fried, E. Hala and O Vilim, Collection Czech. Chem. Commun. 21, 260 (1956).

63. D.T.C. Gillespie, Ind.Eng.Chem. (Anal) 18,
575 (1946).
64. S.R.M. Ellis and B.A. Froome, Chem. and Ind. 237,
(1954).
65. A.F.H. Ward and L. Tordai, Trans. Faraday, Soc., 42,
408 (1946).
66. G. Scatchard and G.M. Wilson, J.Am.Chem.Soc., 86,
133 (1964).

SYNOPSIS OF THE THESIS ENTITLED 'THERMODYNAMIC PROPERTIES OF ALCOHOLS AND ALKOXY ETHANOLS' ~~TO BE~~ SUBMITTED FOR THE DEGREE OF Ph.D (TECH.) (CHEMICAL ENGINEERING) IN THE FACULTY OF TECHNOLOGY OF THE UNIVERSITY OF BOMBAY BY IYER V.NAGARAJAN

Over the years we have accumulated a large amount of useful information about the liquids and solutions. Most of our experimental data are on the properties of liquids such as surface tension, vapour pressure and free energy.

The nature of the liquid-vapour interface can be well understood in the light of the theory of liquids. An adequate description of the surface properties of solutions has been the object of a large body of work beginning with the early papers of Gibbs. Adsorption from solution is an important process technologically, but has received relatively little attention from the fundamental point of view.

Solutions of nonelectrolytes are usually described in terms of activity coefficients which indicate deviation from Raoult's law. Activity coefficient enters as an important parameter in describing equilibrium states. There can be systematic variations in the properties of solutions as the solute is changed within some structurally related family. In order to investigate whether this systematic behaviour occurs with n-alkyl compounds other than alcohols and acids, a study

of the homologous series of n-alkyl ethyleneglycolmonoethers and their aqueous solutions were undertaken.

The first four members of the homologous series $\text{CH}_3(\text{CH}_2)_n\text{-O-CH}_2\text{-CH}_2\text{-OH}$ (where $n = 0, 1, 2$ and 3) were either purified from commercial compounds using a highly efficient spinning band type fractionating column or synthesised in the laboratory and purity tested by the vapour phase chromatographic technique.

The work is divided broadly into two parts. The first part deals with the measurement of surface tension of the pure liquids and their aqueous solutions by the ring detachment method, using a chainomatic balance sensitive to 0.05 mg. Corrections involving the densities of the liquids and the diameters of ring and wire were then applied. From these measurements and the activity values, the excess surface concentrations were calculated using the Gibbs equation. As the activity data for all the systems studied are not available, a reasonable approximate method for calculating the van Laar constants for mixtures of members of a homologous series, from the Parachor values of the pure components and the known constants for any two systems of the series under consideration was used.

From the surface excess value the actual surface concentration for each component was obtained. The test

proposed by Schay and Nagy was applied to the liquid-vapour interface and the adsorbent has been shown to be confined to a monolayer for the systems methoxyethanol-water and ethoxyethanol-water. The applicability of Traube's rule in relation to this homologous series of bifunctional compounds is discussed.

The standard free energy, enthalpy and entropy changes (ΔG , ΔH and ΔS respectively), for the adsorption at the air-water interface of the above alkoxy ethanols from solutions at different concentrations are being calculated using the standard free energy change equation $\Delta G = -RT \ln \Gamma/c$ and the Gibbs-Helmholtz equation which gives ΔH directly from the slope of the ($\Delta G/T$) vs $1/T$ function. The results are being compared with the alcohols.

The second part deals with vapour-liquid equilibrium measurement for the systems methoxy ethanol-water and ethoxy ethanol-water at 65, 80 and 90°C in a modified type of Gillespie still. The activity coefficients were corrected for nonideality and an attempt is being made to calculate the differential molar heats of solution of the solutes in water using the relation between $\log \gamma$ and $1/T$ at constant composition. The values of heat of mixing may be compared with data obtained by direct calorimetry.

ACKNOWLEDGEMENTS

I take this opportunity to express my deep sense of gratitude to Prof. A.B. Biswas, Senior Professor, Indian Institute of Technology, Bombay, formerly Assistant Director, Physical Chemistry Division, The National Chemical Laboratory, Poona, for his inspiring guidance, criticism and helpful suggestions throughout the progress of this work.

During the early stages, I was fortunate to have the enthusiastic co-operation and guidance of Dr. M.K.Gharpurey. Acknowledgement is gratefully given to him.

I am grateful to Dr. S.S. Katti, who has patiently shared with me the absorbing process of learning.

My thanks are due to Dr. L.K. Doraiswamy, and Dr. M.U. Pai from whom I have been able to learn through formal and friendly discussions.

Acknowledgement is also gratefully given to the following persons of Hindusthan Lever Research Centre:

To Dr. S. Varadarajan, Director, for his interest,
to Dr. B.C. Subba Rao for his encouragement and keen interest during the writing of this thesis,
to Dr. G. Srinivasan for very helpful discussions.

I am grateful to Prof. M.M. Sharma, Prof. E.H. Daruwala and Prof. G.M. Nabar of Bombay University for giving me opportunities to do research and to Dr. C. Nanjundayya, Director, The Bombay Textile Research Association, for introducing me to the field of research.

Thanks are also due to the Director, The National Chemical Laboratory, Poona, for allowing me to submit this work in the form of a thesis and to PL-480 authorities for the financial assistance under the scheme 'Investigation on the synthesis and properties of the new type glycol monoalkyl ethers'.

Iyer. V. Nagarajan.

(Iyer V. Nagarajan)