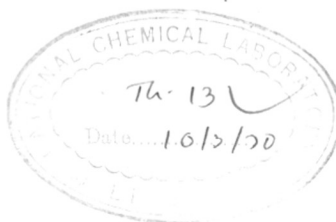


PHYSICO-CHEMICAL PROPERTIES OF FATTY ALCOHOLS  
AND THEIR DERIVATIVES WITH SPECIAL REFERENCE  
TO WATER EVAPORATION CONTROL

COMPUTERISED

A THESIS  
SUBMITTED TO THE  
UNIVERSITY OF BOMBAY  
FOR  
THE DEGREE OF MASTER OF SCIENCE  
IN PHYSICAL CHEMISTRY

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by  
SAMIR PATHAK  
National Chemical Laboratory,  
Poona-8, India.

1968

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## P A R T - II

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P R E F A C E

Surface tension data plays an important role in the interpretation of interfacial properties. Such data were therefore obtained at various temperatures to derive surface thermodynamic quantities of pure liquids and molten solids.

Also the problem of loss of water by evaporation from natural lakes and reservoirs is engaging serious attention particularly in countries situated in arid and semi-arid zones. One of the most promising approaches to minimise the evaporation loss would be by spreading monomolecular layer of various film forming materials over the water surface.

Part-I of this thesis deals with the surface thermodynamic properties derived from surface tension measurements and consists of three chapters. In Chapter-I are presented, relevant informations reported in the literature during the last decade. Methods of synthesis and purification of the compounds (even membered straight chain alcohols from  $C_6$  to  $C_{22}$ , alkoxy ethanols, propanols and butanols from  $C_{16}$  to  $C_{22}$ , Carbitols and cellosolves) along with experimental details of density and surface tension measurements are presented in Chapter-II. The data obtained have been used to calculate thermodynamic properties such as  $L^S$ ,  $\Delta H^S$ ,  $\Delta S^S$  and the results have been discussed in Chapter-III.

Part-II deals with the water evaporation reduction efficacies of various monolayers and is presented in three chapters. We are here particularly concerned with the use of long chain fatty alcohols ( $C_{16}$ - and  $C_{18}$ -OH) prepared from cottonseed oil and their alkoxy ethanol derivatives ( $C_{16}$ - and  $C_{18}$ -OC<sub>2</sub>H<sub>4</sub>OH). A brief survey of research works done in this connection and the semi-field experimental procedure have been described in Chapters-I and II respectively. The evaporation loss data have been collected under various ambient conditions and the results are discussed in the light of their spreading property and equilibrium film pressures at different temperatures in Chapter-III.

I take this opportunity to express my deep sense of gratitude to Dr. S.S. Katti for his able guidance during the course of this work. I am indebted to Prof. A.B. Biswas for his meticulous suggestions and keen interest in the pursuit of the entire work. It is a pleasure to acknowledge with thanks the help rendered by Dr.(Miss) M.V. Natekar in supplying pure alcohols and alkoxy ethanols etc. and Mr. I.V. Nagarajan in setting up few instruments in the initial stages. I wish to thank all my colleagues for their ungrudging cooperation. Finally I wish to thank the Director, National Chemical Laboratory, Poona, for permitting to submit this work in the form of a thesis.

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(SAMIR PATHAK)

P A R T - I

SURFACE THERMODYNAMIC PROPERTIES OF  
ALCOHOLS AND THEIR DERIVATIVES

PART - I

CHAPTER - I

INTRODUCTION

In a programme of studies on the monolayer properties of long chain compounds spread on the surface of water in relation to water evaporation control, a series of compounds of the type  $C_nH_{2n+1}OCH_2CH_2OH$  (where  $n = 16-22$ ) was found to have water evaporation retardation properties superior to cetyl and stearyl alcohols ( $C_{16}H_{33}OH$  and  $C_{18}H_{37}OH$ ) which are normally used for water evaporation control purposes. If an insoluble monolayer is to act as an effective barrier to evaporation, the molecules, among other properties, are required to form a condensed close-packed structure in the monolayer state. The spreading of the substance must be easy and rapid to replenish any part of the film disrupted by wind and some other agencies or it is lost by dissolution or evaporation. Thus film must have rapid self-healing property. The compound must also have high equilibrium spreading pressure to prevent the tendency of disruption and the entry of impurities which may cause reduction in the evaporation resistance by the film.

In this problem we are thus led into the problem of evaluating the spreadability of these compounds over the surface of water. We may briefly mention the criteria of spreading in terms of spreading coefficient. At constant

temperature and pressure, a small change in the surface energy ( $dF$ ) of the system is given by the total differential

$$dF = (\delta F / \delta A_a) dA_a + (\delta F / \delta A_{ab}) dA_{ab} + (\delta F / \delta A_b) dA_b$$

but

$$dA_b = -dA_a = dA_{ab}$$

$$\delta F / \delta A_a = \gamma_a, \quad \delta F / \delta A_b = \gamma_b \quad \text{and} \quad \delta F / \delta A_{ab} = \gamma_{ab}$$

$$\therefore S_{b/a} = \gamma_a - \gamma_b - \gamma_{ab}$$

where  $S_{b/a}$  is called the spreading coefficient for the substance b (of surface tension  $\gamma_b$ ) on substrate a (of surface tension  $\gamma_a$ ).  $\gamma_{ab}$  is the interfacial tension between a and b.

If  $S_{b/a}$  is positive spreading is accompanied by a decrease in free energy, and will occur spontaneously, while if it is negative, the substance b in the form of a liquid will remain as a lens on liquid a.

Another relevant property of a film forming material desired to be known is about the extent of anchorage of the molecule on the water surface, so as to obtain some indication about the resistance offered by the spread film against piling up by the wind on a side of a reservoir. It may conveniently be related to the work of adhesion ( $W_{ab}$ ) given by the expression

$$W_{ab} = \gamma_a + \gamma_b - \gamma_{ab}$$

Thus, in principle, this may be evaluated from the surface tension data. Furthermore, the most commonly measured property of a monolayer, obviously also of particular importance in relation to water evaporation control is the film pressure or surface pressure ( $\pi$ ). This is defined as the difference between the surface tension of the pure liquid ( $\gamma_0$ ) and that of the film covered surface ( $\gamma$ ), i.e.  $\pi = \gamma_0 - \gamma$ .

It was the reduction of the surface tension of a clean water surface which led Pockels, Rayleigh and Langmuir to their conclusion about the nature of the spread films. Therefore, any method of surface tension measurement can, in principle, permit the calculation of  $\pi$  and several other monolayer properties. From the above outline it appears that the surface tension, apart from displaying basic molecular property and free energy of the surface arising, as is well known, due to unbalanced molecular attraction which tends to pull molecules into the interior or the liquid phase, often provides useful informations in problems of applied interest such as in our case on the spreadability of monolayer, it is adhesion to the subphase and surface pressure.

In view of our interest in the monolayer properties of a series of n-fatty alcohols and their alkoxy ethanol derivatives, surface tension data of these series of compounds enter as an important determining factor for

elucidating their behaviour as water evaporation retardants. In this part of the thesis we are presenting their surface tension data in the liquid state. Further, several of the surface thermodynamic properties relating to the equilibrium of surfaces, as can be derived from surface tension data, are also included.

Before presenting the results of our study it is desirable at this stage to briefly mention the concept of surface tension and the various thermodynamic functions used in our calculations and also to give a survey of the related results reported in the literature. The topic of surface tension concerns interfaces and as it deals with the equilibrium configurations, occupies an important place in the general frame work of thermodynamics.

Spontaneous curvature produced at the surface is obviously due to the interactions (inward attraction) between molecules in the surface layer and in the layer contiguous with it. The resultant of all intermolecular attractive forces is normal to the surface and the direction of the phase of greater density. It is this asymmetric force distribution that gives rise to the tensile stress or surface tension.

The space occupied by the molecules only a few molecular diameters below the surface layer upto which molecular attractions are effective in producing the surface

curvature and whose interactions contribute to the total contractile force is designated as the surface region. The potential energy which the molecules possess due to the formation of the surface is the measure of the increase in the work capacity of the system and may be described as the "energy of surface formation".

Formation of a surface is always attended by a cooling effect. Therefore, the quantity of thermal energy which must be supplied during the isothermal formation of the liquid surface region by unit area is the "latent heat of surface formation".

Before the discussion of the molecular and structural picture of the surface region, it is desirable to develop some of the thermodynamic relationship between surface quantities.

In the present work measurements were confined to pure compounds and hence thermodynamics of one component system is applicable for the liquid/gas interface.

In a hypothetical system consisting of some liquid, to uncover an amount of the surface  $dA$ , the work required to do will be  $\gamma dA$ . This is reversible work at constant pressure and temperature and thus gives an increase in the free energy of the system

$$dG = \gamma dA \quad \dots (1)$$



The total free energy of the system is then made up of molal free energy times the total number of moles of the liquid plus  $G^S$ , the surface free energy per unit area times the total surface area. Thus

$$G^S = \gamma = (\delta G / \delta A)_{T,P,N} \dots (2)$$

In the above reversible process the heat associated gives the surface entropy,

$$dq = TdS = TS^S dA$$

where  $S^S$  is the surface entropy per square centimeter of the surface. Now,

$$\begin{aligned} (\delta G / \delta T)_p &= -S \\ \therefore (\delta G^S / \delta T)_p &= -S^S \dots (3) \\ \text{or } (d\gamma / dT) &= -S^S \end{aligned}$$

Finally, the total surface enthalpy per square centimeter

$$H^S = G^S + TS^S$$

$H^S$  and surface energy  $E^S$  are often not distinguished, as a result  $E^S$  is also equal to  $G^S + TS^S$  or

$$\begin{aligned} E^S &= \gamma - Td\gamma/dT \\ &= \gamma + L^S \dots (4) \end{aligned}$$

It is evident from the above that the total surface energy is nothing but the enthalpy of surface formation which involves both the free surface energy and the latent heat of surface formation.

Some of the important factors which lead to the change in the value of surface tension are: curvature of the surface, pressure, electric and magnetic fields etc. An unusual variable is the rotation. Apart from the n-long chain alcohols, the compounds studied in the present work are composed of a long alkyl chain like the alcohols and an extended polar group of the type  $-\text{OCH}_2\text{CH}_2\text{OH}$ ,  $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH}$ ,  $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{OH}$  or  $-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ . They will therefore display properties of rotational isomerism and inter or intra-molecular hydrogen bonding interaction and large changes in sizes and packing of the molecules which may be responsible for unusual changes in the values of surface tension.

A review of the literature shows that experimentation on surface tension and working on the theoretical background was started more than hundred years ago. Important information and new developments are however presented for ready reference.

Rayleigh (1890) and Pockels (1891) were the first to observe the lowering of surface tension due to the contamination of the water surface by films of oils. Later Rayleigh (1899) outlined the phenomenon of the formation of a monomolecular film of the substances spread on water surface due to which a sudden drop in the surface tension value was observed. The surface pressure of a film ( $\Pi$ ) on

the water surface, was then explained by Langmuir, attainment of the maximum value of which lowers the surface tension of water to maximum. In 1925, Rideal enunciated that an increase in the surface concentration of a film (surface pressure) definitely reduces the evaporation of the liquid surface on which it is spread. Posner (1952) measured surface tension and surface potential as functions of concentration and temperature for a homologous series of normal aliphatic alcohols, (C<sub>2</sub>-C<sub>8</sub>). From temperature dependence of the surface tension the quantities  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$  and  $\Delta G^{\circ}$  for the adsorption process were calculated and the molecular configuration in the surface was tentatively deduced.

More recently, Good (1957) proposed surface entropy to be the criteria of surface orientation, and calculated the molar surface entropy from the temperature coefficient of the surface tension. Girifalco in the same year, developed a theoretical relation between free energies of cohesion of separate phases to the free energy of adhesion and hence surface tension to the interfacial tension, and confronted it with experimental data. Roger (1958) fitted his surface tension data on liquid halogen fluoride at various temperatures (T), to the empirical equation  $\gamma = C - DT$  where C and D are the constants, found by the method of least square. While attempting to give an exact expression for the surface tension based on quantum theory, Brout (1958), enunciated

that a thorough knowledge of the bulk properties is sufficient to estimate surface properties well of a quantum fluid.

Jarvis (1959) measured surface tension for various fluorinated compounds. Spreadability of a surface active substance upon liquid substrate, was found to be more pronounced, the greater the differences between their surface tensions and that of the substrate. Jasper (1960) calculated thermodynamic properties from the interfacial tensions between water and halo-alkyl benzenes. He formulated empirical equations leading to the calculation of entropy, enthalpy and latent heat for unit area of the interface.

Steinhardt (1960) derived intermolecular distances and intermolecular association energy for pure non-polar liquids, from surface tension. His expression for surface tension involved  $d$ , the average distances between molecular centres in a liquid. The temperature dependence of surface tension was attributed to the temperature dependence of  $d$ . In case of the discontinuous surfaces, Rusanov (1962), established connection between the variation of surface tension, temperature, pressure, composition of the co-existing phases and the radius of curvature of the discontinuous surface. Fowkes (1962) considered surface tension to be a measure of the attractive forces between the surface layers and liquid phase and that such forces and their contribution to the free energy are additive. He expected surface tension of polar liquids to be made up of two independent

additive terms, for example, in case of water, hydrogen bonding (h) and dispersion forces (w) are the main intermolecular forces as a result  $\gamma = \gamma^h + \gamma^w$ . He evaluated  $\gamma^w$  by taking surface tensions and interfacial tensions of hydrocarbons with water.

Kipling (1962) studied the adsorption of butyl alcohol at the water surface. He presented the adsorption isotherms of fatty alcohols upto octyl alcohol in comparison with that of butyl alcohol. Jasper (1963) measured the interfacial surface pressures, using a vertical-pull filmometer, produced by soluble monolayers of a series of normal alcohols (C<sub>8</sub>-C<sub>12</sub>) at the octane/water interface as the result of positive adsorption. Later in 1965 he reported the thermodynamic properties of soluble monolayers produced by normal alcohols (C<sub>8</sub>-C<sub>12</sub>) at the octane/water interface. He studied the decrease in the free energy of the interface due to absorption of this series of alcohols. With the measurement of surface tension, he calculated entropy, latent heat and enthalpy of adsorption over a temperature and concentration range. The observation of increase in the surface excess with the temperature was attributed to the deviation of the octane solution of the alcohols from ideality. Also, at lower concentrations, he found the interfacial surface pressures to be independent of chain-length.

Eberhardt (1966) presented an equation for the surface tension of binary liquid mixtures, based on the assumption

that the surface tension  $\gamma$ , is a linear function of the surface layer mole fraction. In the same year (1966) Schmidt fitted his surface tension data on benzene-n-hexane and benzene-n-dodecane mixtures over full composition range, to various ideal, regular solution and cell model equations. The density values of the same, were used to calculate excess volume of mixing. Schmidt again in 1967 gave a new equation relating mixture surface tension to the properties of pure components.

Chatterjee (1963) studied the adsorption of a series of short chain ( $C_4$  to  $C_8$ ) acids. He calculated surface pressure ( $\Pi$ ) at each solute concentration from  $\Pi = \gamma_0 - \gamma$  where  $\gamma_0$  and  $\gamma$  are the interfacial tensions of oil/water system in absence and presence of acids respectively. The area  $A$  has been calculated using Gibbs equation  $1/A = -C/kT \cdot d\gamma/dC$ ,  $k$  being Boltzman constant. Schmidt (1963) obtained surface tension and densities of n-hexane-n-dodecane mixtures at various temperatures. The positive excess of surface tension, found in the n-dodecane-n-hexane and n-dodecane-2,2,4, trimethyl pentane system was explained on the basis of position and orientation effects at the liquid/vapour interface. The surface tension of homopolymers above their melting points were measured by Roe (1968) using the pendant drop method. The MacLeod exponent  $p$ , which is usually around 4 for simple liquids, has been found to be smaller, generally between 3 and 3.5, reflecting the

restrictions imposed on the conformation of polymer molecules at the surface.

Using these investigations as guide line, an attempt is made to study the thermodynamic properties of the surface region of alcohols and their various derivatives through the surface tension measurements.

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## PART - I

### CHAPTER - II

#### EXPERIMENTAL

##### Materials

The n-alcohols and n-alkoxy ethanols of shorter carbon chain lengths were obtained in a fairly pure state from commercial sources (B.D.H. or FLUKA make). These were subjected to further purification to obtain a purity better than +99%. Alcohols from C<sub>6</sub>- to C<sub>12</sub>- carbon chain, cellosolves (C<sub>n</sub>-OCH<sub>2</sub>CH<sub>2</sub>OH) and carbitols (C<sub>n</sub>-OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OH) from C<sub>1</sub> to C<sub>4</sub> carbon chains are all liquids at room temperature. These were fractionally distilled several times in a 65 cm. long and 2 cm. diameter column packed with pyrex glass helics. The middle fractions distilling at constant temperatures were collected and checked for purity by vapour phase chromatography using an Aerograph A.350-B. Compounds which are solids at room temperature e.g. alcohols from C<sub>14</sub> to C<sub>22</sub> carbon chain (also obtained from B.D.H.) were first recrystallised repeatedly using dry acetone as the solvent and then subjected to a process of acetylation. The acetates were fractionally distilled followed by deacetylation. The long chain alkoxy ethanols, alkoxy propanols and alkoxy butanols were synthesised by the Williamson's method. This consists of condensing n-alkyl bromides with monosodium



salts of ethane diol, 1.3 propane diol and 1.4, butane diol respectively. They were also purified by the fractional recrystallization followed by fractional distillation in the same distillation column and checked for purity by vapour phase chromatography.

### Density Measurements

The density values determined at the described temperatures, formed new data for only alkoxy-ethanols, -propanols, -butanols and alcohols of C<sub>12</sub> or more carbon chain. The densities of all other compounds, which were reported in the literature, confirmed the purity of the compounds and the consistency of the density measurements. Moreover, the surface tension calculation require the density values of the respective compounds at corresponding temperatures.

A variety of methods for measuring density are reported in the literature, some of the important ones being the specific gravity bottle method, the sinker method and the pycnometer method.

The Lipkins bicapillary pycnometer was adopted by us for it requires a very small quantity of the test liquid and fairly accurate measurements could be made with it.

A special Lipkin type pycnometer was made in the laboratory. This consisted of a U-shaped pyrex capillary having a small bulb at the base of one of its arms. For liquids (at room temperature) capillary bore used was 0.5 mm.

The capacity of the pycnometer including the bulb was approximately 2 ccs. The arm opposite to the one having the bulb was bent at an angle of  $45^{\circ}$  to facilitate easy filling. The total length of the pycnometer did not exceed 9 cms.

#### Cleaning of the Pycnometer

To clean the interior portion of the capillary, it was allowed to stand in contact with a cleaning solution (hot chromic acid) overnight or till the last traces of grease disappeared. To remove adsorbed acid, it was then rinsed repeatedly with distilled water and dried in a vacuum desiccator. A constant weight of the empty pycnometer ensured complete drying.

#### Filling of the Pycnometer

All the compounds which are liquids at room temperature could be conveniently filled up by the syphoning action of the bent capillary. In the case of viscous liquids such as  $C_{12}$  alcohol a mild vacuum was applied. The compounds which are solids at room temperature, were first liquified by heating. The pycnometer was also heated to a suitable temperature and the hot liquid was filled in by applying a mild vacuum and it was placed in the thermostat (adjusted to a required controlled temperature) mounted on a suitable stand.

#### Weighing

Considerable attention was paid to weighing by taking care so that no water or acid vapours were adsorbed in the

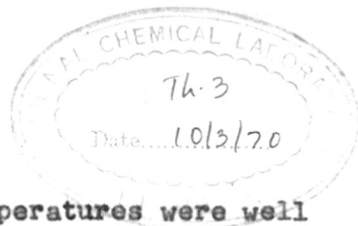
glass vessel or the glass vessel was not electrostatically charged due to friction during wiping. The pycnometer was weighed before and after the filling of the liquid to obtain the mass of the liquid enclosed in it. Buoyancy corrections were not applied, as the results are reported only upto the fourth place of decimal.

#### Precautions

To minimize any change in the volume of the bulb, the pycnometer was not heated or cooled above or below the experimental temperatures excessively. It was never subjected to large pressure differences such as those caused by prolonged evacuation.

#### Calibration and Determination of Density

Density measurements by a pycnometer entails determining the volume of the liquid enclosed in the pycnometer. Therefore the entire capillary tube portion was calibrated initially in terms of height for corresponding volumes enclosed. The pycnometer was filled with double-distilled water taking care that no air bubble was entrapped in it as indicated by the attainment of equal heights in both arms of the capillary. The heights of the water column above the respective reference marks (engraved at the base of the two capillary arms at equal heights above the bulb) were accurately determined with a travelling microscope and the corresponding mass of water enclosed was noted. Accurate



densities of pure water at different temperatures were well established. Therefore the volume of the water enclosed was obtained and a graph of height against volume was plotted. This was a linear curve and hence, for density measurements of test liquids, only the height of the liquid column above the reference marks, in the pycnometer was to be determined along with the mass of the liquid enclosed. From the calibration plot, the volume enclosed was read and thereby the densities were calculated using  $D = M/V$  where  $D$  is the density,  $M$  the mass in gms. and  $V$  the volume in ccs. Calibration graphs were obtained at suitable temperatures in our experimental temperature range. The temperature of the thermostat was controlled within  $\pm 0.05^{\circ}\text{C}$  using water for temperatures below  $50^{\circ}\text{C}$  and glycerol for temperatures above  $50^{\circ}\text{C}$  as the thermostatic liquids.

#### Surface Tension Measurements

Surface tension measurements of pure liquids or molten solids can be made using a variety of techniques as described by Adam and Bikerman. More recently Heller described a new micro method for measuring surface tension of liquids and solutions on samples as small as  $10^{-4}$  ml. The method is based on the inequality of surface pressures of liquid columns contained in a conical capillary. Rijke in 1964 determined surface tension by measuring on a manometer the pressure required to expel the liquid from a narrow pore in a thin glass plate. This method requires



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only two drops of liquid. David Winkil in 1965 discussed the theoretical back ground of the pendant drop method for measuring surface tension. In the same year Hilton described a tensiometer which automatically detaches a platinum stirrup from the liquid/air interface while continuously recording the force exerted by the surface of the liquid. As a result the direct reading of absolute surface tension is possible eliminating the need for the ring correction.

Although the capillary rise method is one of the most accurate methods, it requires a large volume of the test liquid. In the drop weight method an important precaution is to use a tip that has been ground smooth at the end and which is free from any nicks. The drops should be formed slowly.

The maximum bubble pressure method is a quasi-dynamic one in that freshly formed liquid/air interfaces are involved.

The Wilhelmy slide and the ring methods are capable of good precision in the measurement. The pendant drop and the sessile drop are static methods based on the shape of the static drop or bubble. The vibrating jet method is a dynamic method for the measurement of surface tension.

Harkins found the ring detachment method to be the best one for both when long time effects are involved and when they are not, if the measurements are conducted taking

care that the liquid surface is in equilibrium with the saturated vapour. The surface tensions of our series of compounds were measured by this method.

The method consists of determining the minimum weight required to detach a ring from a given liquid surface. The most important part of the set up is the ring which is made up of a platinum iridium wire containing about 10% iridium to give the wire adequate stiffness. The wire was fitted with a stirrup by means of the spot welding, which in turn was attached to a light copper chain going upto the balance. A chainomatic balance sensitive to 0.05 mg. was used for this work. The left pan was removed and a hole was bored right below at the base of the balance through which is passed the copper chain connecting the ring. The test liquid was taken in a clean and dry conical flask having a small mouth (little more than the diameter of the ring = 1.3 cms.) but considerable base area. The flask was held by a clamp planted on a smooth jack so that it could be smoothly moved up and down to make contacts with the liquid. Accurate measurements of the diameter of the ring and that of the wire was an important prerequisite. There are various difficulties involved in making precise measurements by the ring method. Any rigorous theory of the ring method would require,

- (1) that the wire of the ring lie in one plane;
- (2) that the plane of the wire be horizontal;

- (3) that the vessel containing the liquid under test be large enough so that any curvature of the free surface of the liquid would not be great enough to affect the shape of the liquid raised by the ring;
- (4) that the surface of the liquid be free from wave motion;
- (5) that there be no motion of the ring;
- (6) that there be no evaporation and consequent cooling of the surface;
- (7) that the ring be round.

The most important source of error arises from the ring not being horizontal.

#### Method of Measurement

The flask was cleaned with hot chromic acid and the acid was allowed to stand in the flask for fifteen minutes. It was then thoroughly washed with double distilled water and dried by little warming in a low temperature oven. The flask containing the test liquid was allowed to stand in the thermostat at a desired temperature for about half an hour before the measurement. The thermostatic liquids are the same as used for density measurements.

The ring was levelled by suspending it by means of a string over a plane mirror placed on levelling screws within about half a millimeter on the top of the mirror. Looking at the ring and its image at mutually perpendicular directions tilt could be determined and corrected for making horizontal by bending the stirrup. The ring was cleaned by

heating it to red hot on a flame. Now, the ring was attached to the copper wire so that it just hangs on the left arm of the balance over the test liquid surface in the flask already in the thermostat. The weight of the ring suspended in air was determined and taken as zero weight. The flask was now raised slowly to meet the ring ensuring complete wetting.

The balance was then released and weights were gradually added to determine the approximate maximum pull. In check determinations, the beam of the balance was raised and lowered again when the pull was about 10 mg. less than the maximum to ensure into proper position, and the additional weights were added cautiously. The minimum weight was taken as the weight required to make the pointer suddenly move to the left which could not be compensated without detachment of liquid surface from the ring.

### Calculations

The minimum weight required to detach the ring from the surface of the test liquid was used to calculate the volume  $V$  from  $V = m/d$  when  $m$  = mass and  $d$  = density determined at the same temperature. The radius of the ring was already determined accurately, therefore the factor  $R^3/V$  was calculated,  $R$  being the radius of the ring. The ratio  $R/r$  was obtained from the value of  $r$ , the radius of the wire. This factor ( $R/r$ ) was a constant and for our ring it was about 42.8. For different values of  $R^3/V$ , Harkins



correction factor was obtained for a particular R/r value (H2.8) from the Harkins correction table. Surface tension was then given by

$$\gamma = p \times f$$

where  $\gamma$  is the surface tension, p is the force involved in the process of detaching the ring and f is Harkins correction factor. The force p is given by the expression

$$p = mg/4\pi R$$

where m is the minimum weight required to pull out the ring, g is the force due to gravity whose precise value in Poona is 978.59 dynes/cm. and R is the radius of the ring. Weight required to pull out the ring could be detected upto 0.05 milligrams therefore, surface tension values were reported upto second place of decimal.

## PART - I

### CHAPTER - III

#### RESULTS AND DISCUSSION

The liquid surface contracts spontaneously due to a unbalanced force on a surface molecule. This force is directed inwards and there is surface free energy associated with it, which may be related to the work of bringing a molecule from the interior of a liquid to the surface and also the surface tension  $\gamma$ . Considering that this tension is acting in all directions parallel to the surface, the surface energy can also be related to the work done in extending a surface which is pulling with a tension  $\gamma$  dynes/cm. or ergs/sq.cm. Provided the surface is of the same nature and structure, the work done in extending it will be definite. If there is any variation observed in surface tension values, it may be related to the variation in size and packing of the molecules and in intermolecular forces. For a homologous series of organic compounds, we may expect the surface tension to increase systematically with increasing molecular weight. Our surface tension data for the different series of related compounds may be examined keeping the above factors in view.

We are presenting our results on surface tension studies in the temperature range of 25<sup>o</sup>-95<sup>o</sup>C of normal alcohols (C<sub>n</sub>-OH with n varying from 6 to 22, comprising of even members

only), alkoxy ethanols ( $C_n-OCH_2CH_2OH$ ,  $n = 1$  to 4 and 16 to 22), alkoxy propanols ( $C_n-OCH_2CH_2CH_2OH$ ,  $n = 16$  to 22), alkoxy butanols ( $C_n-OCH_2CH_2CH_2CH_2OH$ ,  $n = 16$  and 18) and carbitols ( $C_n-OCH_2CH_2OCH_2CH_2OH$ ,  $n = 1$  to 4). Some of the thermodynamic properties such as latent heat of surface formation  $L^S$ , entropy of surface formation  $\Delta S^S$  and enthalpy of surface formation  $\Delta H^S$  derived from surface tension data have also been presented and discussed.

At this stage it should be mentioned that measurements have been limited to those few compounds of a series, which were readily available in our laboratory. It is, however, realised that these limited data severely restrict any definite correlation of the results and conclusions to be made unless studies are made of a more complete series of compounds, which we have in aim to do in due course.

#### Normal Alcohols ( $C_n-OH$ )

The  $\gamma$  values at different temperatures and the derived thermodynamic quantities  $L^S$ ,  $\Delta H^S$  and  $\Delta S^S$  are presented in Tables-IA, IB and IC. The  $\gamma$  and  $L^S$  values are also plotted graphically in Figures I, II and III with respect to temperature and chainlength.

Comparing  $\gamma$  with respect to  $C_n$  (number of carbon atoms in the hydrocarbon chain) in the homologous series (Fig. III) at all the temperatures of the measurements, it is clear that  $\gamma$  more or less linearly increases from  $C_6$  upto  $C_{12}$ , decreases sharply at  $C_{14}$  and then steadily

SURFACE TENSION AGAINST TEMPERATURE  
PLOT OF ALCOHOLS FOR  
VARIOUS CHAIN LENGTHS  
FROM C<sub>6</sub> TO C<sub>18</sub>

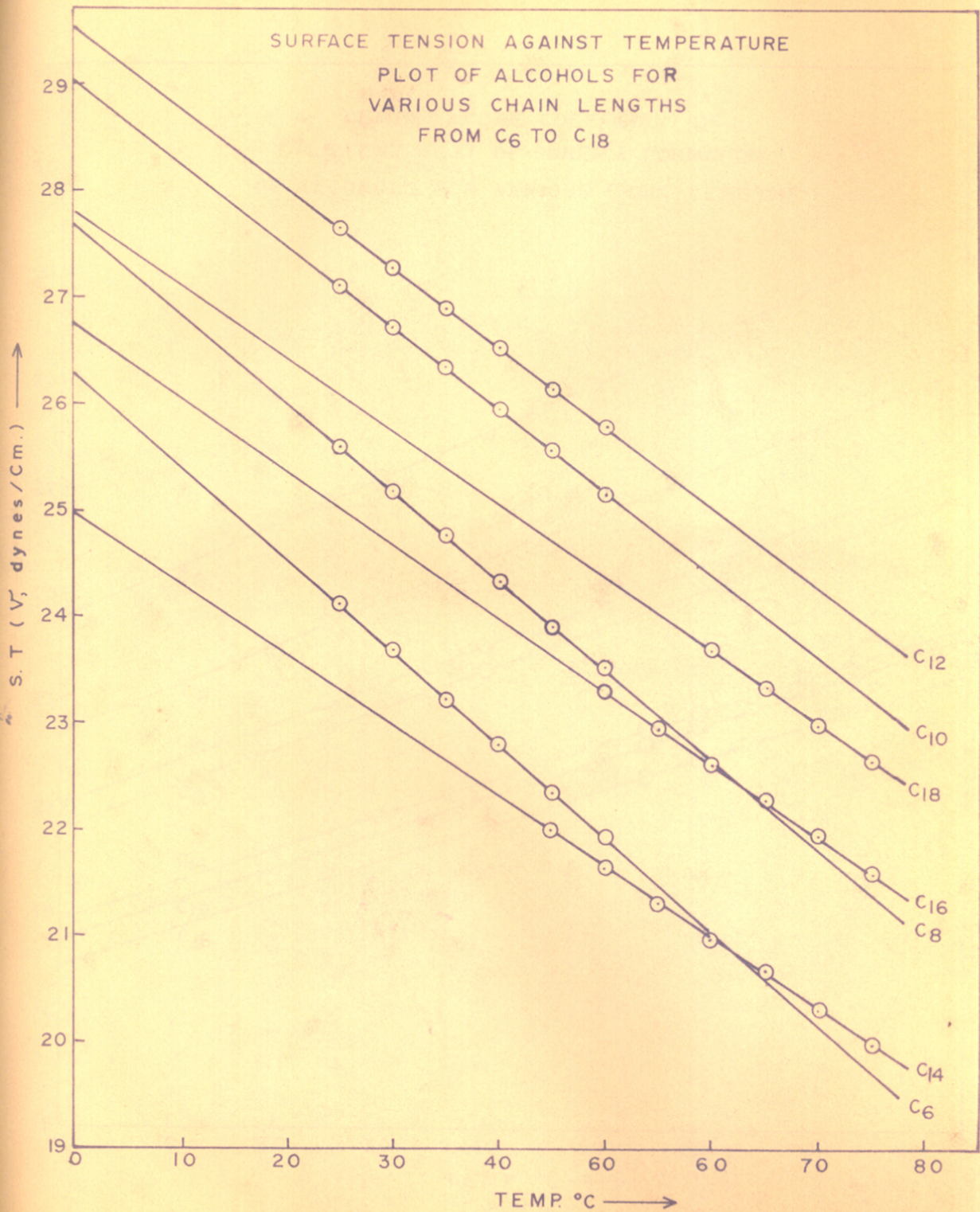


Fig. I



TEMPERATURE COEFFICIENT OF  
LATENT HEAT OF SURFACE FORMATION  
OF ALCOHOLS FOR VARIOUS CHAIN LENGTHS

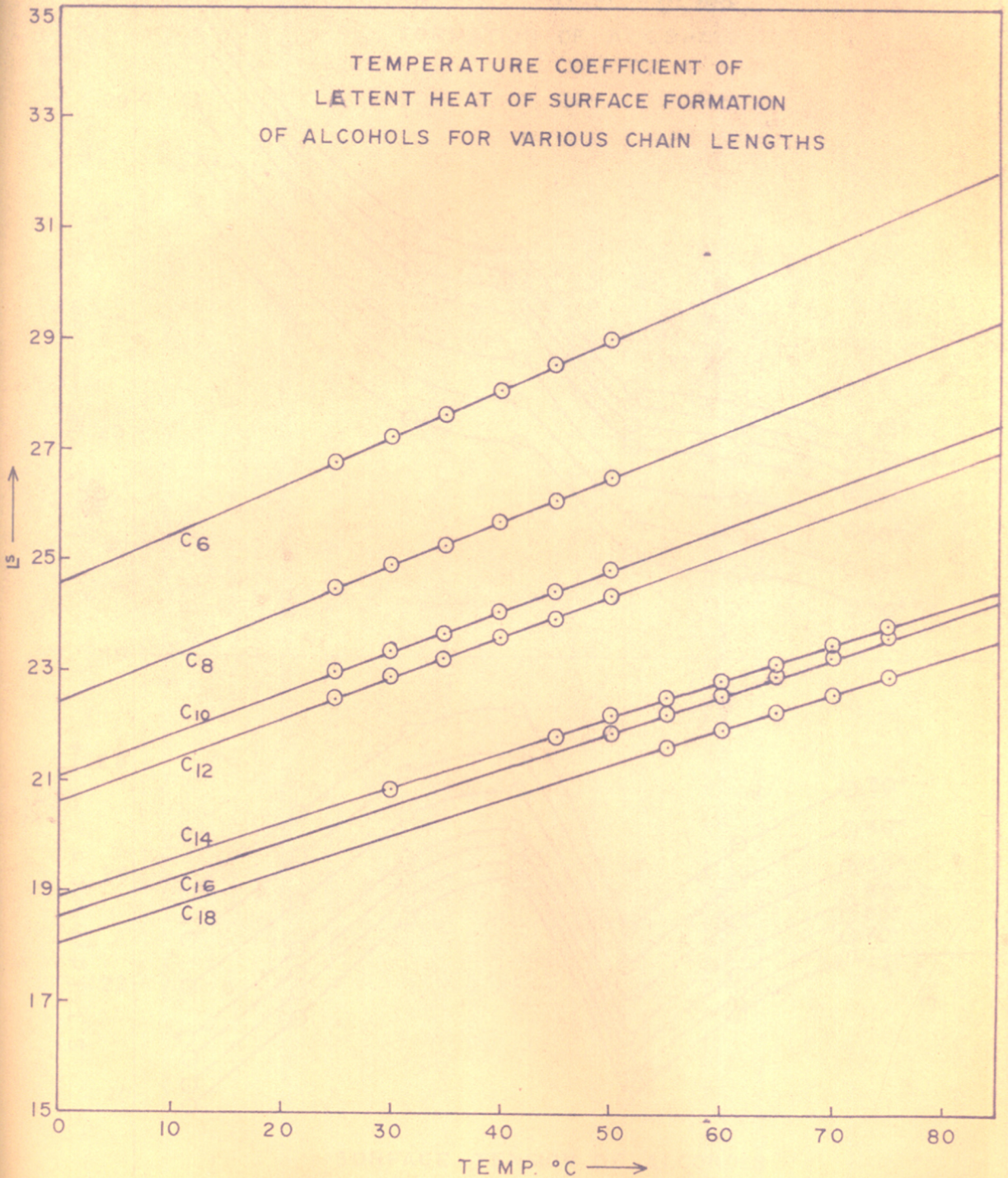


FIG. II



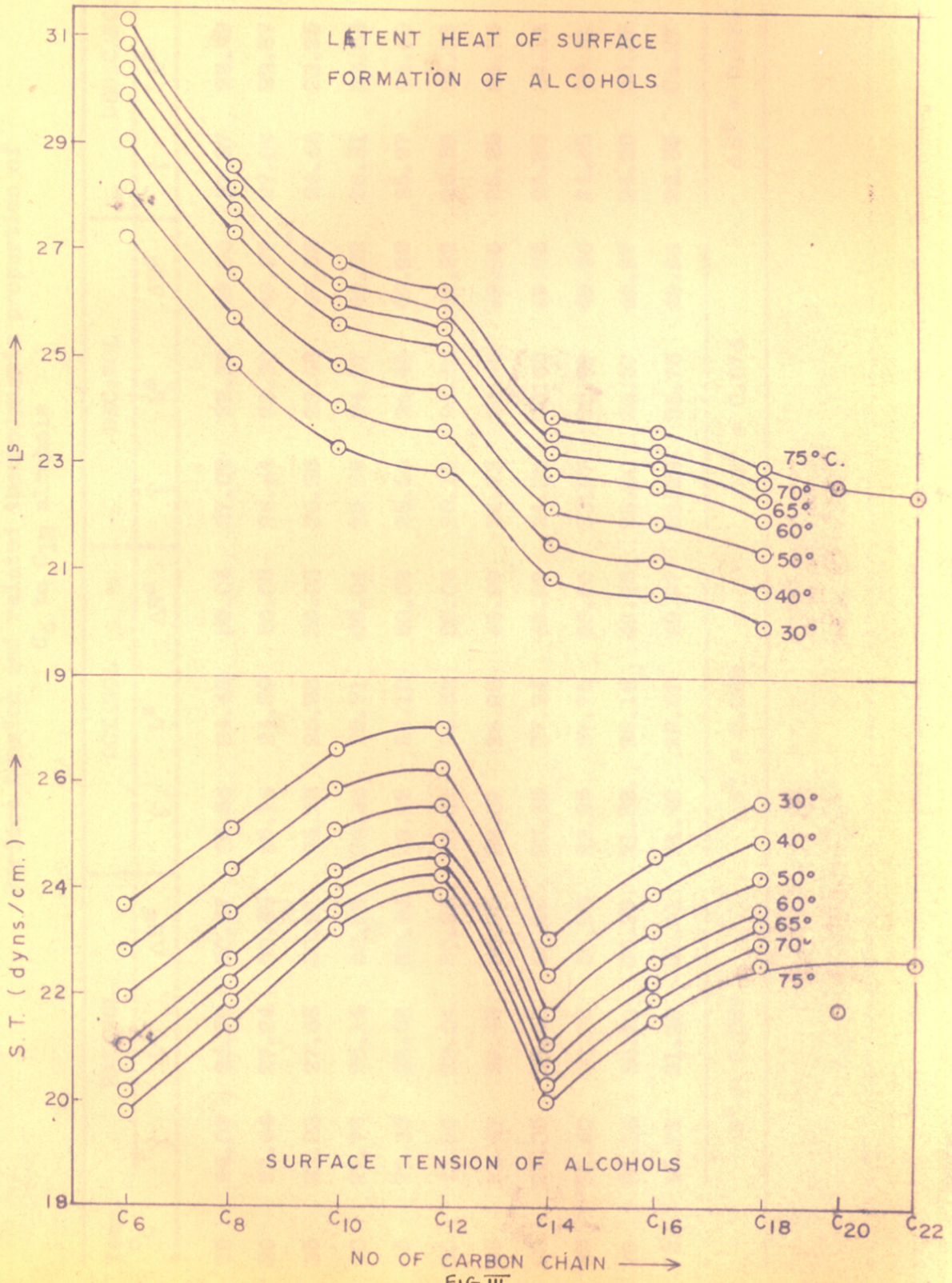


FIG. III

TABLE - IA

Surface tension and related thermodynamic properties of  
C<sub>6</sub> to C<sub>12</sub> alcohols

Temp. °C	HEXANOL			OCTANOL			DECANOL			DODECANOL				
	$\gamma$	Ls	$\Delta H^s$	$\gamma$	Ls	$\Delta H^s$	$\gamma$	Ls	$\Delta H^s$	$\gamma$	Ls	$\Delta H^s$		
25	24.08	26.79	50.87	25.56	24.43	50.04	27.02	22.93	49.96	27.37	22.49	49.86		
30	23.64	27.24	50.88	25.16	24.89	50.05	26.64	23.30	49.97	27.09	22.87	49.96		
35	23.23	27.68	50.91	24.75	25.28	50.03	26.25	23.68	49.93	26.66	23.25	49.91		
40	22.78	28.14	50.92	24.33	25.71	50.04	25.89	24.07	49.82	26.31	23.63	49.93		
45	22.35	28.58	50.93	23.92	26.10	50.02	25.50	24.45	49.95	25.97	24.00	49.97		
50	21.90	29.04	50.94	23.51	26.53	50.04	25.10	24.83	49.92	25.59	24.38	49.97		
55	21.47	29.48	50.95	23.07	26.92	49.99	24.73	25.22	49.95	25.25	24.75	50.01		
60	21.05	29.93	50.98	22.65	27.34	49.99	24.35	25.60	49.95	24.90	25.14	49.94		
65	20.60	30.38	50.98	22.25	27.75	50.00	23.97	25.99	49.96	24.55	25.51	50.06		
70	20.16	30.83	50.99	21.82	28.16	49.98	23.60	26.37	49.97	24.20	25.89	50.09		
75	19.73	31.28	51.01	21.40	28.57	49.97	23.23	26.76	49.96	23.85	26.27	50.12		
			$\Delta S^s = 0.089$			$\Delta S^s = 0.082$			$\Delta S^s = 0.076$			$\Delta S^s = 0.075$		

TABLE - IB

Surface tension and related thermodynamic properties of  
C<sub>14</sub>, C<sub>16</sub> and C<sub>18</sub> alcohols

Temp. °C	TETRADECANOL		HEXADECANOL		OCTADECANOL				
	$\gamma$	L <sup>s</sup>	$\gamma$	L <sup>s</sup>	$\gamma$	L <sup>s</sup>			
25	23.39	20.47	43.86	24.97	20.23	45.10	25.97	19.66	45.63
30	23.05	20.81	43.86	24.65	20.57	45.22	25.65	19.99	45.64
35	22.71	21.15	43.86	24.30	20.91	45.21	25.30	20.32	45.62
40	22.37	21.50	43.87	23.95	21.25	45.20	24.96	20.65	45.61
45	22.02	21.85	43.87	23.61	21.59	45.20	24.62	20.98	45.60
50	21.67	22.19	43.86	23.27	21.93	45.20	24.30	21.31	45.61
55	21.35	22.53	43.88	22.95	22.27	44.76	23.97	21.64	45.61
60	21.02	22.88	43.89	22.64	22.61	45.25	23.64	21.98	45.62
65	20.65	23.22	43.89	22.24	22.95	45.19	23.31	22.31	45.61
70	20.32	23.56	43.88	21.90	23.29	45.19	22.98	22.64	45.61
75	19.99	23.90	43.89	21.57	23.63	45.20	22.64	22.97	45.61
		$\Delta S^s = 0.068$		$\Delta S^s = 0.067$		$\Delta S^s = 0.066$			



TABLE - IC

Surface tension and related thermodynamic quantities of  
C<sub>20</sub> and C<sub>22</sub> alcohols

Temp. °C	EICOSANOL			DCCOSANOL		
	$\gamma$	L <sup>s</sup>	$\Delta H^s$	$\gamma$	L <sup>s</sup>	$\Delta H^s$
75	21.15	22.79	43.94	21.82	22.45	44.27
85	20.49	23.43	43.92	21.17	23.12	44.29
95	19.84	24.09	43.93	20.53	23.75	44.28

$\Delta S^s = 0.065$                        $\Delta S^s = 0.064$

increases upto  $C_{22}$ , the rate of increase after  $C_{13}$ , however being comparatively low.

It may be supposed from the observed trends that the surface structure remains almost the same below  $C_{12}$ , the steady increase in this region being the effect of both increased size (molecular weight) and chain-chain interaction (van der Waal's attractive force). The fall in surface tension beyond  $C_{12}$  may be attributed to an appreciable change in the surface structure in these liquids, which may have been brought about due to the operation of several factors.

These alcohol molecules are characterised by having a much longer non-polar (hydrocarbon) chain with a small polar (OH) end group. When we consider the lower members of the series at the relevant temperatures in the liquid state, the molecules may be assumed to be in a rather turbulent (disordered) state with rapid interchange of molecules between various positions, in the bulk as also in the surface region. These motions will decrease with increase in the molecular weight at a particular temperature. Further, we may consider the operation of, mainly, three types of intermolecular interactions: (1) hydrogen bonding attractive interaction at the polar end (OH), (2) van der Waal's type attractive interaction between the long hydrocarbon chains, (3) dipole-dipole repulsive

interaction between similarly charged atoms ( $O^-$  and  $H^+$ ) present in the polar group.

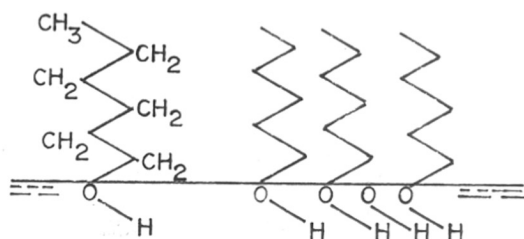
For the lower members of the series, due to the possible random motion and consequent disordered state of the molecules the chain-chain distance ( $r$ ) will be comparatively large and van der Waal's force being inversely dependent on the seventh power of the intermolecular distance ( $r^7$ ) will be weak. On the other hand, this type of molecules can readily form hydrogen bonded structure

$$\left( \begin{array}{c} R \\ \diagdown \\ O-H \end{array} \dots \dots \begin{array}{c} R \\ \diagdown \\ O-H \end{array} \right)$$

which will be facilitated if the neighbouring molecules are suitably oriented so as to enable formation of a linear  $O-H \dots O$  arrangement. Thus many of the molecules can approach each other with an inclined (approximately horizontal) orientation of the chain such as to facilitate the formation of linear  $O-H \dots O$  hydrogen bond in the case of lower members. The strength of this  $O-H \dots O$  bond decreases with its deviation from the linearity. Thus on an over all basis when the molecules are in a random orientation in these liquids, associative hydrogen bonding interaction would exist to some extent. This, in effect, may be considered as a further increase in the size (mol. wt.) by association producing an increase in the surface tension value for the system, such as we observe for the members of this series below  $C_{12}$ .

As the chainlength further increases, the chain-chain (attractive) interaction will increase, at some

stage they may have an over-riding tendency to assume an ordered configuration where the chains will have parallel orientation to maximise the van der Waal's term. These long chain molecules in the liquid state are particularly well known to form oriented crystal-like arrangement (which are often called 'liquid crystals') in which molecules pack themselves closely in a parallel manner with the polar groups at one side. At the surface of the liquid the molecules are known to be vertically oriented with the hydrocarbon chain projecting out in the vapour phase (air), as depicted below:



This type of arrangement will make the hydrogen bonding interaction quite weak due to unfavourable (angular) O-H....O arrangement. Further, as mentioned above, since the van der Waal's force decreases with about  $r^{-7}$ , only the nearest neighbour interaction will be of importance. This situation gives rise to considerable rotational freedom around the chain axis of the molecules. This has been experimentally observed in spectroscopic and dielectric studies of these systems. Comparing the disordered structure where stronger hydrogen bonding interaction is partially formed, with that when the liquid crystalline structure is formed, it is realised that in

the latter case less amount of work in extending the surface will be required which in effect will give rise to lower surface tension. The sharp fall in surface tension in the region  $C_{12}$ - $C_{14}$  may be attributed to the onset of the formation of ordered and stable liquid crystalline structure as indicated above.

A similar phenomenon has also been observed in the case of soluble surface active agents such as lauryl sulphate ( $C_{12}$ ). When several of the measured physical properties of their aqueous solutions (surface tension, electrical conductivity) are plotted against concentration, a sharp break is seen at a point which is called the critical micelle concentration (CMC). This discontinuity is taken to indicate the formation of micelle with ordered (lamellar) structure by the association of long chain molecules in the solution. It has been found that with molecules having lower-chainlength ( $C_{12}$  chain), the C.M.C. is very high (tendency to micelle formation is much weaker) whereas the C.M.C. decreases appreciably as the chain length increases (the tendency to micelle formation is stronger).

Beyond  $C_{14}$ -OH, we find that the surface tension values steadily increase. Here, the surface structures and packings may be considered to be more or less the same, but the size of the molecules gradually increases as also the van der Waal's interaction. Hence surface

tension values will increase as we actually observed. The gradual decrease in the rate of increase of surface tension tends to reach a steady value because the percent change in the above factor as we ascend the series (provided similar surface structure is retained) becomes smaller and hence the observed variations between near neighbours are smaller.

The  $C_{20}$ -OH gave an appreciably lower value than expected. Since the compound was not extremely pure, we are not sure whether the measured value is abnormal due to a characteristic difference in its structural feature or it is an experimental artifact due to the presence of some surface active impurities. However, it may be mentioned in this connection that Davies (1965) also obtained anomalously large values in his heat of sublimation measurements of  $C_{20}$ -OH, which we attributed to traces of olefinic impurities in the alcohol. Comparing the results of the same measurements on different compounds of  $C_{20}$  chainlength, he also thought of the possibility of the  $C_{20}$ -chain adopting some special configuration in the gaseous state.

Alkoxy Ethanols or Cellosolves ( $C_n$ -OCH<sub>2</sub>CH<sub>2</sub>OH)

As mentioned earlier we have carried out measurements for compounds with  $n = 1, 2, 4, 16, 18, 20$  and  $22$  and the results are presented in Tables - IIA, IIB.

TABLE - IIA

Surface tension and related thermodynamic quantities of  
methyl, ethyl and butyl cellosolve

Temp. °C	METHYL CELLOSOLVE			ETHYL CELLOSOLVE			BUTYL CELLOSOLVE				
	$\gamma$	Ls	$\Delta H^s$	$\gamma$	Ls	$\Delta H^s$	$\gamma$	Ls	$\Delta H^s$		
30	30.02	30.91	60.93	27.67	27.72	55.39	26.98	23.63	50.61		
35	29.50	31.42	60.92	27.20	28.18	55.38	26.57	24.02	50.59		
40	28.97	31.93	60.90	26.75	28.64	55.39	26.23	24.41	50.64		
45	28.48	32.44	60.92	26.27	29.09	55.36	25.82	24.80	50.62		
50	27.98	32.95	60.93	25.84	29.55	55.39	25.42	25.19	50.61		
			$\Delta S^s = 0.102$			$\Delta S^s = 0.091$			$\Delta S^s = 0.078$		

TABLE - IIB

Surface tension and related thermodynamic quantities

Temp. °C	ALKOXY ETHANOLS												
	C16		C18		C20		C22		C20		C22		
	γ	ΔH <sup>s</sup>	γ	ΔH <sup>s</sup>	γ	ΔH <sup>s</sup>	γ	ΔH <sup>s</sup>	γ	ΔH <sup>s</sup>	γ	ΔH <sup>s</sup>	
45	26.36	22.42	49.28										
55	26.15	23.12	49.27	21.42	21.98	43.40							
65	25.45	23.83	49.28	20.74	22.65	43.39							
75	24.76	24.53	49.29	20.08	23.32	43.40	27.57	22.97	50.54	21.01	22.45	43.46	
85	24.05	25.24	49.29	19.41	23.99	43.40	26.91	23.63	50.54	20.36	23.09	43.45	
95	23.35	25.94	49.29	18.74	24.66	43.40	26.25	24.29	50.54	19.72	23.74	43.46	

$\Delta S^s = 0.070$

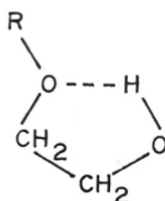
$\Delta S^s = 0.067$

$\Delta S^s = 0.066$

$\Delta S^s = 0.064$



It is seen in Table-IIA that surface tension values slightly decrease as we ascend the homologous series, the change from  $C_2^-$  to  $C_4^-$  is much smaller than that from  $C_1^-$  to  $C_2^-$  cellosolves. Here also we may analyse the results in terms of the factors such as size, packing and intermolecular forces. According to the size and intermolecular (dispersion or van der Waals) force considerations, the surface tension values should have increased with increase in size, in contrast to what we observe. However, the nature of the molecules is different here in that they can form both intra- and intermolecular hydrogen bonds. In the case of longer chain molecules such as  $C_{16}^-$ ,  $C_{18}^-$   $OCH_2CH_2OH$ , Srinivasan (1966) has recently shown from infrared absorption studies that they exist in both gauche and trans configuration in the liquid state, the former arising from intramolecular hydrogen bond formation as shown below.



Thus the dimension of the polar group becomes quite large as to appreciably lower the packing density or increase the average intermolecular distance and consequently reduce the intermolecular force. Hence the surface tension values may decrease for  $C_2^-$  and  $C_4^-$ -compounds due to the formation of such type of structures with greater

facility for the higher members. However, it may be considered premature to venture into such interpretation without analysing more extensive and reliable data.

Considering the results in Table-IIB, the surface tension value decreases from  $C_{16}$ - to  $C_{18}$ -compound with a slight increase for the  $C_{22}$ -compound. It is again surprising to find that  $C_{20}$ -compound shows an abnormal result, the surface tension values being appreciably higher than its near neighbours on both sides of the series. Leaving it aside, the decrease observed from  $C_{16}$ - to  $C_{18}$ -compound may be analysed on basis of the difference in their packings rather than that of the size.

It is interesting to note (Table-IIC) that the lower members of the series with much shorter chainlength ( $C_1$ -,  $C_2$ -, compared to  $C_{16}$ -,  $C_{18}$ -) show higher values of surface tension. On the basis of size and chain-chain interaction the values of surface tension were expected to be higher for the longer chain compounds. The dominant influence of the formation of hydrogen bonded structure in the former system compared to the formation of ordered liquid crystalline structure by the higher members seems to be well displayed in the observed surface tension values.

#### Alkoxy Propanols ( $C_n$ -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH)

The measured surface tension values of the three propanols (n = 16, 18 and 22) are given in Table-III.

TABLE - IIC

Surface tensions of alkoxy ethanols

Temperature °C	CHAINLENGTH						
	C1	C2	C4	C16	C18	C20	C22
65	26.48	24.55	24.22	25.45	20.74	28.23	21.66
75	25.48	23.69	23.42	24.76	20.08	27.57	21.01

TABLE - III

Surface tension and related thermodynamic quantities of  
C<sub>16</sub>, C<sub>18</sub> and C<sub>22</sub> alkoxy propanols

Temp. °C	C <sub>16</sub>		C <sub>18</sub>		C <sub>22</sub>	
	γ	L <sup>s</sup> ΔH <sup>s</sup>	γ	L <sup>s</sup> ΔH <sup>s</sup>	γ	L <sup>s</sup> ΔH <sup>s</sup>
45	21.53	24.64 46.17				
55	20.76	25.42 46.18	21.99	24.76 46.75		
65	19.93	26.19 46.17	21.24	25.52 46.76		
75	19.20	26.97 46.17	20.48	26.27 46.75	27.26	23.66 50.92
85	18.43	27.74 46.17	19.72	27.03 46.75	26.59	24.34 50.93
95	17.65	28.52 46.17	18.97	27.78 46.75	25.90	25.02 50.92
$\Delta S^s = 0.077$ $\Delta S^s = 0.075$ $\Delta S^s = 0.068$						

It is seen that surface tension value increases only slightly from  $C_{16}^-$  to  $C_{18}^-$ -compound which seem to indicate that there is little change in the packing and structure of the molecules in the liquid state. The little increase in surface tension may thus be due to the size effect. The  $C_{22}^-$  compound seems to show a little higher rise in the value than that expected in the light of the results shown by the two lower members ( $C_{16}^-$  and  $C_{18}^-$ ). Thus an appreciable change in its configuration and packing in the liquid state may have occurred.

Alkoxy Butanols ( $C_n-OCH_2CH_2CH_2CH_2OH$ )

The surface tension values for  $C_{16}^-$  and  $C_{18}^-$ -compounds are given in Table-IV. A slight decrease in going from  $C_{16}$  to  $C_{18}^-$  is observed, which may be attributed to a difference in their configurations in the liquid state. It appears that the overall intermolecular force is higher with the shorter chain molecule.

Carbitols ( $C_n-OCH_2CH_2OCH_2CH_2OH$ )

It may be seen (Table-V) in this series of compounds (with  $n = 1, 2$  and  $4$ ) that the surface tension values indicate slight increase from  $C_1^-$  to  $C_2^-$ , but from  $C_2^-$  to  $C_4^-$  the values decrease appreciably at all the temperatures measured. As before we may assume that there is little change in the structure and packing of the molecules in the former case, whereas the packing must have changed

TABLE - IV

Surface tension and related thermodynamic quantities of  
C<sub>16</sub> and C<sub>18</sub> alkoxy butanols

Temp. °C	C <sub>16</sub>			C <sub>18</sub>		
	$\gamma$	L <sup>s</sup>	$\Delta H^s$	$\gamma$	L <sup>s</sup>	$\Delta H^s$
50	22.31	20.99	43.40			
55	22.00	21.32	43.32	21.91	19.63	41.59
60	21.68	21.64	43.32	21.61	19.98	41.59
65	21.35	21.97	43.32	21.31	20.28	41.59
75	20.69	22.65	43.34	20.70	20.88	41.58
85	20.02	23.31	43.33	20.10	21.47	41.57
95	19.40	23.92	43.32	19.52	22.08	41.60

$\Delta S^s = 0.065$

$\Delta S^s = 0.060$

TABLE - V

Surface tension and related thermodynamic quantities of methyl, ethyl and butyl carbitol

Temp. °C	METHYL CARBITOL			ETHYL CARBITOL			BUTYL CARBITOL		
	$\gamma$	L <sup>s</sup>	$\Delta H^s$	$\gamma$	L <sup>s</sup>	$\Delta H^s$	$\gamma$	L <sup>s</sup>	$\Delta H^s$
25	28.49	13.37	41.86	29.53	21.09	50.63	25.01	16.92	41.94
30	28.23	13.59	41.82	29.17	21.45	50.62	24.72	17.21	41.93
35	28.03	13.82	41.85	28.83	21.80	50.64	24.45	17.49	41.94
40	27.81	14.04	41.86	28.46	22.16	50.62	24.16	17.77	41.96
45	27.57	14.27	41.84	28.10	22.51	50.61	24.03	18.06	42.06
50	27.35	14.49	41.84	27.76	22.86	50.63	23.59	18.34	41.94
-----									
$\Delta S^s = 0.044$			$\Delta S^s = 0.070$			$\Delta S^s = 0.056$			

considerably either through hydrogen bonding interaction or change in molecular configuration in going from  $C_2$ - to  $C_4$ -compound.

The Rate of Change of Surface Tension ( $d\gamma/dT$ )

The values of  $d\gamma/dT$  for different series of compounds in the temperature range of  $25^\circ$  to  $95^\circ C$  have been presented in Table-VI.

The surface tension values for all the liquids generally decrease with increase of temperature i.e.  $d\gamma/dT$  is negative, due to expansion of the surface region where upon the intermolecular distance increases and the attractive force between neighbouring molecules decreases. In the treatment by Lennard-Jones and Carner (1940), the sign of  $d\gamma/dT$  depends on that of  $\ln(v/v_s)$  where  $v$  and  $v_s$  are the free volumes for the liquid in bulk and in the surface region respectively. Ordinarily,  $v_s$  is greater than  $v$  and thus the term is negative. It may, however, be mentioned that for some metals such as copper and iron,  $d\gamma/dT$  has been found to be positive. It has been suggested that due to the electric field, the surface region may be contracted (Sapski, 1948) which would make  $d\gamma/dT$  positive.

Molecules spontaneously orient themselves in the liquid surface in such a way as to decrease the interphasal discontinuity and formation of the liquid surface region is attended by a decrease in the entropy. The surface entropy may therefore be regarded as a criterion of molecular



TABLE - VI

Entropy of surface formation  $\Delta S^s$  (dY/dT)

Compound	C <sub>6</sub>	C <sub>8</sub>	C <sub>10</sub>	C <sub>12</sub>	C <sub>14</sub>	C <sub>16</sub>	C <sub>18</sub>	C <sub>20</sub>	C <sub>22</sub>
Alcohols	0.089	0.082	0.076	0.075	0.068	0.067	0.066	0.065	0.061
	----- C <sub>1</sub> C <sub>2</sub> -----		----- C <sub>4</sub> -----						
Alkoxy ethanols	0.102	0.091	0.073	-	-	0.070	0.067	0.066	0.064
Alkoxy propanols	-	-	-	-	-	0.077	0.075	-	0.068
Alkoxy butanols	-	-	-	-	-	0.065	0.060	-	-
	----- C <sub>1</sub> C <sub>2</sub> -----		----- C <sub>4</sub> -----						
Carbitols	0.044	0.070	0.056	-	-	-	-	-	-

orientation, which as mentioned earlier is given by

$$\frac{d\bar{Y}}{dT} (= \Delta S^S).$$

$d\bar{Y}/dT$  decreased gradually as the molecular weight increased for all the series of compounds studied. In case of alcohols, entropy decreased right from  $C_6$ - upto  $C_{22}$ - alcohol. The decrease is quite rapid at the beginning but reaches almost a limiting value of about 0.065 at  $C_{14}$  carbon chain which does not alter much upto  $C_{22}$ . This seems to indicate the attainment of an ordered orientation of the molecules at the surface of the long chain alcohols completely.

Similar results were obtained by Adam (1941) from a study of the homologous series of hydrocarbons, acids, amines and triglycerides when  $d\bar{Y}/dT$  showed a decrease with increase in molecular weight, as also the attainment of a limiting value of about 0.07 when the chains are about 10 carbons long.

Alkoxy ethanols, alkoxy propanols and alkoxy butanols showed decrease in entropy with increasing carbon chain. The carbittols of  $C_1$  to  $C_4$  carbon chain showed anomalous values of entropy which can not be definitely explained without the knowledge of similar data on more members of the same series.

Entropy increases from alcohol to alkoxy ethanol and further to alkoxy propanol when equal hydrocarbon chain-lengths are compared. Ethanols and propanols carry a ether

type oxygen which might introduce intramolecular hydrogen bonding leading to modified structure. Thus the degree of order is less in case of alkoxy ethanols and alkoxy propanols than that of alcohols due to the operation of the dipole-dipole repulsion factor to a greater extent, which resulted in weaker intermolecular force and resultant increase in the degree of disorder. The lower melting point of the alkoxy ethanols compared to the corresponding alcohols may be taken as indication of the existence of weaker intermolecular force in them. A slight decrease of entropy for alkoxy butanols as compared to alcohols was observed. The alkoxy butanols being bulky molecules as compared to alcohols, it may be presumed that their bulk imparts a degree of order on them, effective enough to show lesser entropy values than alcohols.

Total Surface Energy  $E^s$  ( $\Delta H^s$ )

The enthalpy of surface formation or the total surface values are reported in Table-VII for all the series of compounds in the temperature range of 25°-95°C.

Enthalpy ( $E^s$  or  $\Delta H^s$ ) being the sum of two oppositely varying quantities  $\gamma$  and  $L^s$  as indicated earlier remains independent of temperature for all the compounds studied in the said temperature range.

In the homologous series of alcohols as also in alkoxy ethanols the lower members showed higher values of enthalpy as compared to the higher ones. This follows

TABLE - VII

Enthalpy of surface formation  $\Delta H^s$  (E<sup>s</sup>)

Compound	C <sub>6</sub>	C <sub>8</sub>	C <sub>10</sub>	C <sub>12</sub>	C <sub>14</sub>	C <sub>16</sub>	C <sub>18</sub>	C <sub>20</sub>	C <sub>22</sub>
Alcohols	50.79	50.11	50.14	50.15	43.85	45.25	45.79	43.92	44.29
	-----								
	C <sub>1</sub>	C <sub>2</sub>	C <sub>4</sub>						
Alkoxy ethanols	60.92	55.36	50.62	-	-	49.29	43.40	50.54	43.45
Alkoxy propanols	-	-	-	-	-	46.17	46.75	-	50.93
Alkoxy butanols	-	-	-	-	-	43.32	41.58	-	-
	-----								
	C <sub>1</sub>	C <sub>2</sub>	C <sub>4</sub>						
Carbitols	41.86	50.63	41.94	-	-	-	-	-	-

from the higher values of entropy and shown by these compounds. Enthalpy increases from C<sub>16</sub> to C<sub>22</sub> carbon chain in alkoxy propanols whereas it decreases from C<sub>16</sub> to C<sub>18</sub> in alkoxy butanols. Comparing the three carbitols studied, ethyl carbitol was found to show higher values of enthalpy than those of methyl and butyl.

The trend of changes in the enthalpy values with respect to chainlength or in going from one substituting group to another can not be analysed in terms of the molecular orientation and force, without a more complete study on individual homologous series.

The linear variation of  $\gamma$  and  $L^S$  with temperature can be expressed by the following

$$\gamma = a - bt \quad \dots (5)$$

and

$$L^S = c + dt \quad \dots (6)$$

where  $t$  is the temperature. The specific constants  $a, b, c$  and  $d$  are presented in Table-ID. Putting the values of  $\gamma$  and  $L^S$  in terms of specific constants, an empirical relation for the calculation of  $\Delta H^S$  at any temperature could be presented i.e.

$$\Delta H^S = a + c + t(d-b) \quad \dots (7)$$

Actually, a more linear relation is obtained when  $\gamma(m/d)^{\frac{2}{3}}$  is plotted. Thus,

$$\gamma(m/d)^{\frac{2}{3}} = K(T_c - T)$$

TABLE - ID

Specific constants obtained from equations (5) and (6)

Compounds	a	b	c	d
Hexanol	26.24	0.089	24.55	0.089
Octanol	27.66	0.082	22.45	0.082
Decanol	29.04	0.077	21.10	0.079
Dodecanol	29.55	0.075	20.60	0.075
Tetradecanol	25.00	0.069	18.85	0.068
Hexadecanol	26.75	0.068	18.50	0.068
Octadecanol	27.79	0.066	18.00	0.067

This was attributed by Eötvös according to whom the value of constant  $K$  is nearly 2.1 ergs/degree for most liquids, except the associated ones which should show this value less than 2 ergs/degree. Although Eötvös law may not be entirely valid, all our compounds being associating type, did show values of  $K$  less than 2 ergs/degree.

#### Density Measurements

The density values of the long chain alcohols, alkoxy ethanols, alkoxy propanols and alkoxy butanols which have not been reported in the literature so far are summarised in Table-VIII.

TABLE - VIII

## Densities

ALCOHOLS		ALKOXY ETHANOLS		ALKOXY PROPANOLS		ALKOXY BUTANOLS	
Temp. °C	Density gms./cc.	Temp. °C	Density gms./cc.	Temp. °C	Density gms./cc.	Temp. °C	Density gms./cc.
C <sub>20</sub>	75 0.8059	C <sub>16</sub>	45 0.8491	C <sub>16</sub>	45 0.8506	C <sub>16</sub>	50 0.8469
	85 0.7987		50 0.8447		50 0.8475		55 0.8436
	95 0.7919		55 0.8418		55 0.8445		60 0.8404
							65 0.8371
C <sub>22</sub>	75 0.8063	C <sub>18</sub>	55 0.8473	C <sub>18</sub>	55 0.8423	C <sub>18</sub>	55 0.8443
	85 0.7986		60 0.8432		60 0.8395		60 0.8412
	95 0.7911		65 0.8392		65 0.8362		65 0.8374
		C <sub>20</sub>	75 0.8059	C <sub>22</sub>	75 0.8297		
			85 0.7987		85 0.8208		
			95 0.7919		95 0.8134		
		C <sub>22</sub>	75 0.8255				
			85 0.8186				
			95 0.8119				



P A R T - I I

WATER EVAPORATION CONTROL

BY MONOLAYERS

## PART - II

### CHAPTER - I

#### INTRODUCTION

In recent years the problem of loss of water by evaporation from natural and artificial storages such as lakes and reservoirs, has drawn considerable attention in many countries. More particularly, this is a dominant problem for countries situated in arid and semi-arid zones. Koenig (Chemical Week, 1955) from the U.S.A. says that Texas loses as much water from reservoir evaporation as it consumes every year. In Australia, where there are large areas desperately short of water, normal evaporation losses amount to fall in water level in a reservoir by as much as 8 feet annually (SwRI, 1956), an amount often larger than that available for use. Similar statistics of water loss is heard of from various parts of Europe (SwRI, 1956), Africa and countries like Malaya, Indonesia and India. Accordingly, investigations have been undertaken in many countries to determine ways and means of minimizing the evaporation loss. One of the most promising ways of reducing mass transfer coefficient of water through the interface, seems to be covering the entire surface of water in the reservoir with a thin insoluble layer of some compounds. The 'layer' would be acting as a barrier,

restricting escape of water molecules through the interface and would thereby minimise the loss of water by evaporation. As early as in 1899 the film forming abilities of certain organic compounds was observed. Attempts to use such film forming material as water evaporation retardants were made in 1924 onwards. It was Rideal (1925) who successfully enunciated that evaporation through film covered surfaces is much less than that through clean water surface.

The material forming a film on the surface of water has to satisfy a number of conditions e.g.

1. It should form a close-packed, incompressible and stable film with facility.
2. It should have high equilibrium spreading pressure. This will prevent disruption of the film and resist the entry of deleterious impurities which may reduce the evaporation resistance of the film.
3. It must have reasonably high rate of spreading to facilitate the formation of the film and also to heal up the film if damaged due to some extraneous causes or lost by evaporation or dissolution in the subphase water.
4. It must allow the passage of sunlight and diffusion of oxygen so that stored water will not become stagnant and the biological life is not disturbed.
5. It should also have strong anchorage on the surface of water so that the film is not easily pushed to one side of the reservoir by wind and piled up.
6. The film must be elastic. That is it should expand and contract when waves are formed on the water surface or due to ambient temperature variation, without any break.

Considering all these factors, the n-long chain fatty alcohols such as cetyl and stearyl alcohols were found to be suitable ones and accordingly extensive studies have been made to evaluate their suitability for the purpose.

As early as in 1917 Langmuir studied the spreading behaviour of oily films. Experimenting with the moving barrier method, he suggested that the forces which cause the spreading are due to an attraction between the molecules of the oil and those of water. Harton in the same year gave an empirical formula for the rate of evaporation. Giblet in 1921 discussed various parameters affecting evaporation e.g. wind velocity, humidity and water temperature. Understanding the natural process of distribution of the water vapours evaporated was imperative, he felt. In 1924, Himus and Hinchley performed experiments of water evaporation from copper pans under varying wind velocities. They verified the formula viz.  $W = [(P_e - P_d)/50]^{1.2}$  where  $P_e$  = vapour pressure of water in pans,  $P_d$  = vapour pressure in air and  $W$  = rate of evaporation. Further,  $W = a(P_e - P_d)$  where  $a$  is a coefficient varying only with wind velocity. Hedestrand in 1924 while trying to interpret theoretically the effect of oily contamination noted that the surface properties of water are altered, by reducing surface tension. A decrease in surface tension means a decrease in attractive forces between water molecules in the surface, which may accelerate evaporation. It was however shown that such effect does not occur with close-packed oil films because resistance is offered at the air/water interface

which water molecules have to overcome before passing into gas phase. Rideal (1925), one of the pioneers in the field, described in 1925 the efficiency of monolayers as evaporation retardants. He observed that an increase in the surface concentration or film pressure retards the rate of evaporation. Both condensed and expanded films exhibited these characteristics. In the same year Adam (1925) tried to determine the difference in the rates of evaporation from clean and film covered surfaces. In condensed films, molecules are closely packed and are strongly attracted to the surface water molecules and this non-volatile, insoluble film would therefore, hinder evaporation. He disagreed with Hedestrand (1924) that the lowering of the surface tension accelerates evaporation. On the contrary, according to him a decrease in the surface tension means an increase in the compression of the film. Cummings (1927) theoretically deduced evaporation from the first law of thermodynamics. Ramdas (1927) revealed the far reaching effects of monomolecular films on the water surface. In 1937 Baranaev in the U.S.S.R. studied some effects of insoluble monolayers on evaporation reduction. Adam (1937) described a rapid method of determining the surface pressure depending on the spreading property of some compounds on non-spreading ones. Docking (1940) obtained about 50-60 % reduction of evaporation with paraffin oil. They experimented with various oils among which high boiling natural oil of vertical retort tar gave about 99%

evaporation reduction. They however could not obtain stability of the multimolecular films of hydrocarbons spread by amphipathic molecules adsorbed in the interface. Reduction of evaporation was found to be greater in windy conditions than in still air. DuNouy (1944) observed definite lowering of the rate of evaporation by monolayers. Maisel (1950) explained that the nature of turbulence in the moving stream will affect the rate of transfer between phases. Mansfield in his observation in 1953 said that a fluid duplex film reverts to an equilibrium state comprising of a monolayer and lenses of oil. In the latter form it offers less resistance to evaporation whereas rigid Duplex films are fractured rapidly by wind and dust. Reduction of evaporation leads to an increase in surface temperature and accordingly a compensating effect is sufficient to destroy the potential efficacy of the film. The effect of an increase in the wind velocity according to him is to decrease the rate of absolute evaporation. In another observation (1955) he suggested that accommodation coefficient of monolayers increase with temperature. In a semi-field experiment with 1.5' diameter and 3' high pans he was able to save 0.5' of water using cetyl alcohol. He observed a temperature difference of about 2-3°C between the film covered pan and the control. The maximum reduction obtained was about 48%. Archer (1955) recognized a contamination effect on which the retardation of evaporation is strongly dependent. The specific rate of evaporation was

explained as the reciprocal of the specific rate constant for condensation through films. Durham in 1957 opined that evaporation reduction increases with the dosage of the film forming compound. He performed some petri-dish experiments with 90% cetyl alcohol and determined absolute loss in mass of water. As the dosage increases a maximum reduction is obtained when the film is about 7 molecules thick with an area/molecule of  $20 \times 10^{-16} \text{ cm}^2$ . By about the same time Ramdas (1957) investigated evaporation from water surface covered with cetyl alcohol as a function of temperature. The efficiency of the film was shown to be less when it is in the liquid or gaseous form at higher temperature than when it is in less compressible solid-like form as at lower temperature. Grundy (1957) reported a practicable method of dispensing, in large lakes, beads of cetyl alcohol in gauze windowed floating containers as spreading instrument which also served as the reservoir for replenishment of the films and this maintained the efficacy for several months. A solution of commercial cetyl alcohol in pet-ether (B.P. 95-160°C) containing 7% ethyl alcohol was used for casting the films. Grundy (1957) further reported the use of kerosene (paraffin oil) as a spreading solvent for effective evaporation reduction by cetyl alcohol. Durham (1957) tested the efficiency of blends of commercially available cetyl and stearyl alcohols through petri dish experiments. These blends were found to be more efficacious as compared to pure alcohols themselves as water evaporation retardants. The higher rate of spreading of such

mixtures than the corresponding pure components was further improved by adding 5 to 8% oleyl alcohol. These films also showed better self healing property. Mansfield (1957) indicated that the formation of monolayers from beads depends as much on perimeter/area ratio as on the bead structure. The crystalline bead spreads faster than amorphous ones. During the year 1958 Dressler presented an economic evaluation of the evaporation control methods based on results obtained in parts of America. In 1958 La Mer established that the evaporation resistance of monolayers is affected to an appreciable extent by the nature of the spreading solvent. Benzene, for instance, was shown to have deleterious effect due to the holes formed in the cast film by the slow evaporation of the solvent molecules occluded in the monolayers. Mansfield (1959) estimated the influence of depth of stored water upon the annual evaporative cycle of a water storage. He also correlated storage evaporation and losses from an evaporimeter. The nature of ravages of wind, wave and dust upon the monolayers spread upon exposed surfaces of water. La Mer (1959) felt that the evaporation resistance of monolayer is independent of the spreading technique and much more sensitive to impurities in the sample than are most of the usual physical and chemical tests that are normally used as criteria of purity. A number of stearic acid samples from different sources showed remarkable diminution in resistance to evaporation depending on amounts of the impurities present particularly



at low surface pressures. In order to demonstrate the effect of contamination on monolayers, La Mer and Barnes (1960) studied various mixed monolayers. When  $C_{13}$  alcohol was contaminated with  $C_{12}$  alcohol, the latter molecules could be squeezed out of the monolayer on compression and then the mixture behaved like pure  $C_{13}$  alcohol whereas  $C_{14}$  alcohol did not come out on compression and as a result, the evaporation reduction was lowered. Vines (1960) described the dusting method of spreading over large areas. Water surface is treated from a boat by dusting it with a fine, dry cetyl alcohol powder. An effective cover is quickly obtained in calm weather. Deo et al. have reported a new series of compounds for water evaporation reduction in 1960. These glycol mono-alkyl ethers (alkoxy ethanols) have been found to be superior evaporation retardants to the corresponding n-fatty alcohols. In 1962 and 1964 Katti compared the evaporation reduction efficacies of these alcohols (n-long chain) and alkoxy ethanols and their mixtures. A significant difference in their efficacies during the day and the night was observed. In 1963 Shukla studied the efficacies of  $C_{14}$ ,  $C_{16}$ ,  $C_{18}$  and  $C_{22}$  alcohols and the corresponding alkoxy ethanols at different relevant temperatures. Ramdas (1966) reviewed the various aspects of reduction of evaporation by these types of monolayers. Starting with insoluble and soluble monolayers he studied surface contamination, surface movement, surface pressure, area and rate of spreading, optical and general physical

and chemical properties of surfaces and surface films. He concluded that the cost of saving 1,000 gallons of water is indeed less than the rates at which the municipalities in many cities supply water. Shukla (1966) observed that reduction efficacies of the various alcohols and alkoxy ethanol mixtures increase at lower temperature because the films are more condensed and compact at those temperatures. McArthur (1966) felt the use of fatty alcohols effective but a continuous generation of the film was needed as the film on reservoirs deteriorates or gets destroyed by many factors such as bacteria, wind and dust. The rate of spreading of cetyl alcohol is reduced by wetting, for it spreads from triple interface of air/solid/water and by wetting this interface is reduced. Bose (1966) reported better efficacy of ceto-stearyl alcohol mixture, octadecoxy ethanol and its mixture with stearyl alcohol in four feet diameter evaporimeter experiments. Katti (1966) tested n-long chain alcohols, alkoxy ethanols and their mixtures in different combinations. Alkoxy ethanols proved to be much better evaporation retardants. Garstka (1966) presented the results of investigations of the Bureau of Reclamation in the U.S.A. where the problem of evaporation from reservoirs has been carefully analysed. The various modes of evaporation reduction are discussed and the use of surface films approved as the best and effective method for the purpose. Chowdhury (1966) conducted various experiments on the water evaporation retardation efficiency

of cetyl alcohol and  $C_{18}$  glycol ether in the Rajasthan desert. They studied the effect of very high wind velocity, bombardment of the films with sand and dust and various methods of spreading the films. Mihara (1966) reported some performances of octadecoxy ethanol as evaporation retardant. Bursztyn (1966) found two shortcomings of monolayers, firstly, monolayers cause increase of vapour pressure leading to their rupture and secondly, many monolayers are attacked by bacteria. He found solid paraffin with white reflective pigment acts as efficient evaporation retardant. Noe (1967) made comparative studies on odd and even carbon chain alcohols. He obtained a linear relationship between percent water saving and carbon chain length.

#### Object of the Present Work

It has been well established in earlier studies but mostly through experiments in the laboratory that the monolayers of n-alkoxy ethanols of the type  $CH_3-(CH_2)_{n-1}OCH_2CH_2OH$  (designated as  $C_n-OC_2H_4OH$ ) are much superior evaporation retardants to the corresponding n-fatty alcohols (designated as  $C_n-OH$ ). These resistances are often very sensitive to impurities and ambient conditions. However, in practical application in lakes and reservoirs, we may have to sacrifice to some extent the stringent purity conditions in favour of lower cost of the material. Therefore, experiments with mixed films and with those products of graded purity as prepared in the laboratory simulating the

commercial production conditions, are very desirable. Furthermore it may sometime happen that some impurity present in the commercial compound are too difficult to remove or cannot even be detected with usual laboratory physical chemical tests; but harmful effect, if any, on the film properties due to their presence even in small quantities has to be evaluated.

We have also observed that evaporation resistance and related results obtained under semi-field conditions are much more useful for evaluating the efficacies of these films for better correlation with field experiments.

In view of the above, in a project on the study of water evaporation control by insoluble monolayer, we have prepared several fatty alcohols such as  $C_{16}$ -OH and  $C_{18}$ -OH by hydrogenolysis of appropriate vegetable oils namely cottonseed oil. The products obtained at different stages of purification have used in our semi-field experiments as described later. The corresponding alkoxy ethanols such as  $C_{16}$  or  $C_{18}$ - $OC_2H_4OH$  would commercially be prepared by ethylene oxide condensation when, along with the desired monoglycol product some quantity of di- and tri-glycol condensed products may also be produced even under carefully controlled conditions. Similar studies as indicated above for the alcohols have also been made. The purest products are prepared by different methods as described later and experimented with for comparison purposes.

In addition to the above, the corresponding n-alkoxy propanols and n-alkoxy butanols have also been prepared and studied with a view to determine the effect of addition of these groups at the end of the chain in comparison with those of alcohols and ethanols.

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## PART - II

### CHAPTER - II

#### EXPERIMENTAL

##### Material

The compounds used to form monolayers for evaporation resistance studies, e.g. n-alcohols, alkoxy ethanols, alkoxy propanols of C<sub>16</sub>, C<sub>18</sub> and C<sub>22</sub> carbon chain and alkoxy butanols of C<sub>16</sub> and C<sub>18</sub> carbon chain, have all been prepared in our laboratory. They were further purified by recrystallization from acetone solution and subsequently by fractional distillation as described in Chapter-II, Part-I, of this thesis. Compounds showing about 95% purity were considered pure enough for our semi-field experiments. Alkoxy ethanols, propanols and butanols were synthesised by condensation of n-alkyl bromides with mono-sodium salts of ethane diol, 1,3 propane diol and 1,4 butane diol respectively. Vegetable oils are the chief sources of long chain alcohols. We have therefore chosen cottonseed oil for obtaining mixtures of C<sub>16</sub> and C<sub>18</sub> alcohols. Alkoxy ethanol mixtures were obtained by the same method using alcohol mixtures obtained by direct hydrogenolysis of cottonseed oil. The ethylene oxide condensation of the alcohols were conducted to obtain alkoxy ethanols at lower costs, during which a product consisting of mixtures of unreacted alcohols, and about 20% mono-condensate (alkoxy ethanols) along with poly-condensates depending on the molar proportions of



SEMI-FIELD EXPERIMENTAL SET UP

ethylene oxide to alcohol was obtained. The mixture of alcohols obtained from hydrogenolysis of cottonseed oil were converted to bromides and by Williamson's syntheses, to corresponding mixtures of alkoxy ethanols. Synthetic mixtures of alcohols and alkoxy ethanols were prepared from the pure components in the same proportion as those obtained from oil hydrogenolysis products and ethylene oxide condensations.

#### Semi-field Experiments

Evaporimeter pans, made of galvanised iron sheets fifteen in number were installed in an open lawn in our laboratory. Eleven of them were used with film covered surface, remaining four as control (without film) so that eleven compositions were screened at a time. The pans were of 1.2 meter diameter and 0.45 meter height availing a total water surface area of about 1.13 sq. meters. Each pan contained about 54 litres of water and were placed on cement bases about 0.60 meter above the ground. Every pan was provided with a funnel holding bracket which was also used to clamp the film pressure balance. The funnels had diameters of 0.18 meter and its end was kept sufficiently below the water surface so that while water was added to the pans for adjustment of the level the film was least disturbed. An arrangement for placing a thermometer was also provided to read the temperature of the water surface. The pans were coated with thin layers of aluminium paint



frequently to prevent them from getting rusted and contaminating the water. The main pan was connected to another small side-pan through an opening of the bottom. This side-pan was also made of galvanised iron sheets having a diameter of 0.38 meter and of the same height. It was enclosed in a heavily lagged wooden box and mounted on levelling screws. The heavy lagging minimises exchange of heat with the surroundings. Every small pan had a side opening which led into a glass cylinder having an arrangement to place a spherometer on the top of it. The level of water is noted at the glass cylinder with a spherometer for the level of water was same in both bigger and smaller pans. The whole system was found very satisfactory in damping the fluctuations in water levels caused by ripples and waves, if produced on the surface of water in the larger pan by wind. The change in the water level could be measured accurately down to 0.01 mm. The design of the insulated small pans which is also called "Athavle type" open pan evaporimeters was adapted from Agri. Met. Technical Circular No.14, Meteorological Office, Poona, 1946. A site was chosen in the garden taking care to see that no tall trees or constructions were nearby, so that the area received clear sun-light and unobstructed flow of wind. The possibility of dry leaves or other dirt falling from the trees were also thereby reduced. Weather conditions were noted at the site. Anemometers were fitted at various corners of the enclosed area parallel to every row of pans

to record the wind velocity. Maximum and minimum thermometers and dry bulb and wet bulb thermometers (for relative humidity) were placed in a Stevensons screen located at the side of the pans.

### Spreading

The film forming materials were spread on the water surface in the form of solutions. They were dissolved in freshly distilled petroleum ether (65°C to 70°C) so as to make a 2.5% solution and when spread on the surface of the water, the solvent (Pet. ether) evaporates off leaving behind an insoluble, compact evaporation resistant film.

Initially the pans were thoroughly washed and filled with normal tap water. For a short while the pans were slowly overflowed with water to obtain a clean water surface and a little (about 2 ml.) evaporation retarder solution was added to the water surface in the appropriate pans to remove any dirt on the surface. Again when the water level was being adjusted down to a suitable level of about 7 cms. from the brim of the pans, more retarder solution (about 2 ml.) was added so that any adventitious contaminants may not spread on the water surface. Finally, after equilibrium was attained in all the pans, about 4 ml. of the retarder solution was added and spherometer reading was taken. In all 8 ml. of 2.5 % solution of evaporation retarding material was added, which amounted to about 30-40 times the amount theoretically required to cover the surface with a close-packed monolayer.

### Calibration of the Pans

Absolute water evaporation from all the pans were noted simultaneously for calibration. Being made up of same material and having the same dimensions, the error due to thermal expansion of the pan due to variation of ambient temperatures was neglected. The purpose of this type of experiment was also to determine the particular water levels in various pans on adjustment to which the water evaporation for a given interval of time under similar conditions remains the same with an experimental error of about 2%. These levels were noted as standard and since separate spherometers were used for each pan, these levels were represented as standard spherometer readings. To start the experiment every time the water levels were adjusted to these levels.

Two types of experiments were conducted. In the first type, the durabilities of different films were tested and the second type, the effect of every day replenishment of the film with respect to water evaporation retardation efficacy was determined.

### Durability Test

After having cleaned the pans as usual, all the pans were overflowed with water and solutions of the film forming materials were spread in appropriate pans as described earlier. Eleven film covered pans were arranged in four

groups keeping one pan as control one in each group. To start with, the initial spherometer readings were taken and all the meteorological equipments adjusted. Twice a day all these measurements were recorded: Once at 9 A.M. and again at 5 P.M. thereby dividing the span of 24 hours into two intervals. The first interval of 8 hours from 9 A.M. to 5 P.M. was chosen to be called as the "Day time". During this time air as well as water temperature was comparatively high, relative humidity was low and generally the wind velocity was more. The maximum temperature of the day was attained during this time. The evaporation reduction obtained during the day-time was accordingly called the day-time reduction. The second interval was that of 16 hours from 5 P.M. to 9 A.M. next day. The air and water temperatures during this time were lower as compared to the day-time. The minimum temperature of the day was attained during this interval and average wind velocity as well as the relative humidity were lower and higher respectively than the day-time. This duration was called as the "Night time" and the evaporation reduction as night-time reduction.

A third interval was that of 24 hours from 9 A.M. to 9 A.M. in the next day. The actual efficacy of a film was counted on the basis of its performance with respect to number of days.

The 'day-time reduction' and 'night-time reduction' were determined to check any difference in evaporation

rates shown by the films during the day and night period.

In the durability test the retarder solution was added at the beginning of the experiment and its performance was noted every-day without disturbing the films till its resistance were below 10%. The percent evaporation reduction for every film was calculated and relevent meteorological data noted every-day. The efficacy of each film therefore, could be represented by plotting percent evaporation reduction against number of days as in a table. The durability test is important for understanding the stabilities of the various films.

#### Everyday Replenishment Test

The spreading technique as well as the starting of the experiment remains same in every day replenishment test: noting the spherometer and anemometer readings, humidity and the temperatures as in the durability test. As before the 'day-time reduction' and 'night-time reduction' were also noted, but at the end of every 24 hours i.e. at 9 A.M. every morning 4 ml. of 2.5% solution of the evaporation retarder solution was freshly added. The purpose was to replace the film lost due to dissolution or evaporation or piling up. The fresh addition revived partially the efficacy of the films as a result they continued to be efficient for more number of days as compared to the durability test. Experiments were generally continued for five to six days. In field experiments for reducing evaporation

loss of water from reservoirs by spreading monolayers, the retarder material is generally added at regular intervals for replenishing the films. It was therefore desirable to collect performance data on the film efficiency for a number of days at a stretch and also after daily addition of the solution to the evaporimeter pans.

#### Adjustment of Levels

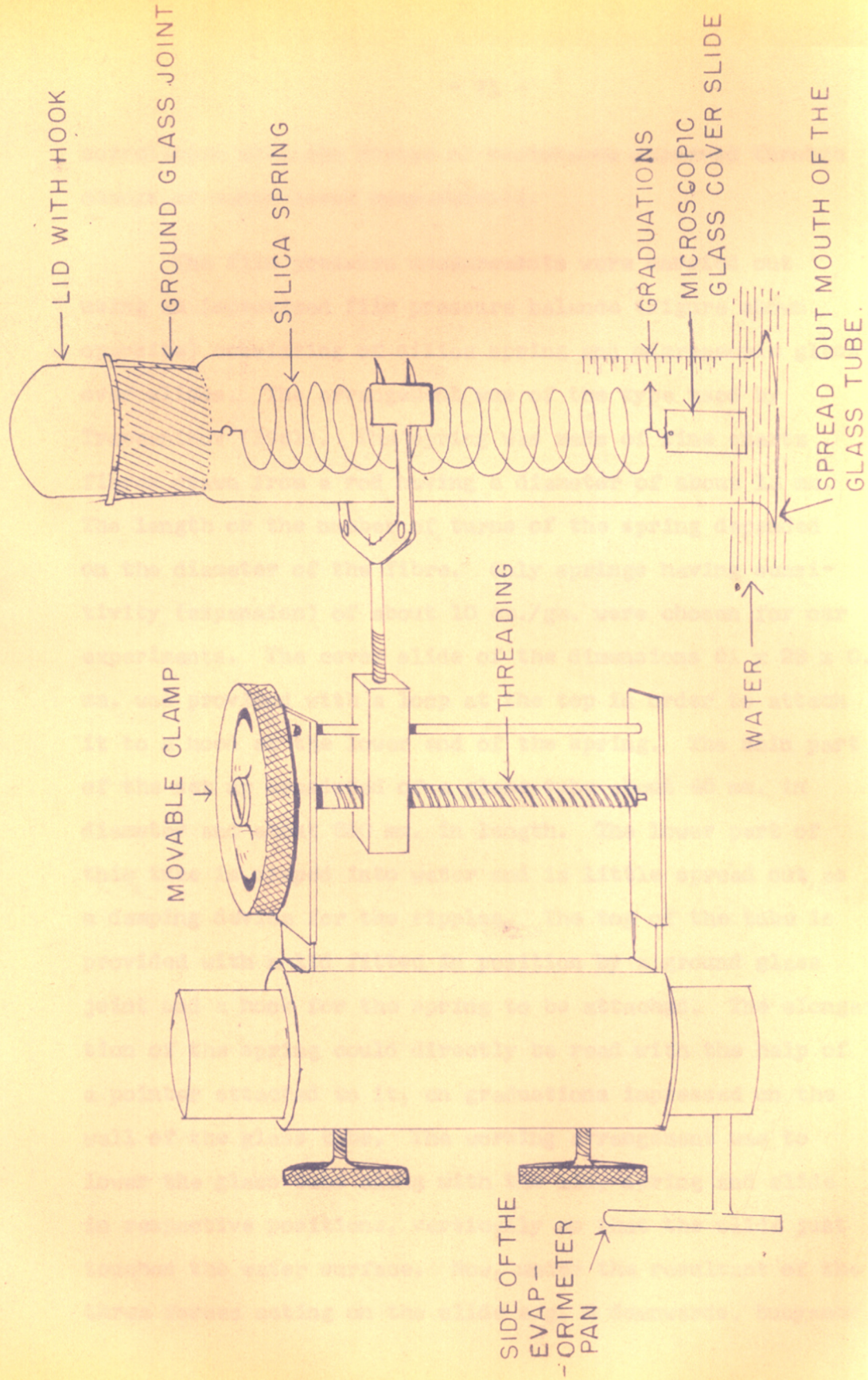
In both types of experiments, the water levels were required to be adjusted, to maintain it within the range of calibration and limit of the spherometer. 1 mm. difference in water level was found to be caused by addition or removal of 1.2 litres of water. Accordingly, after every 24 hours, water required in litres to adjust the water level to the desired level was added and the experiments continued.

#### Film Pressure Measurement

The film pressure or in other words the equilibrium spreading pressure and the efficacy of a monomolecular film are directly related. The higher the film pressure, the higher is the efficiency of a film as evaporation retardant. Although equilibrium spreading pressure of any film does not attain its original value even at the moment of spreading under semi-field conditions and an accurate measurement of the same being not possible, a fair idea of whatever is happening to the film should be collected by the film pressure measurements under semi-field condition for



# FILM PRESSURE BALANCE.



correlation with the change of resistance observed through change of water level measurements.

The film pressure measurements were carried out using an improvised film pressure balance (Figure shown opposite) consisting of silica spring and microscopic glass over slides. The arrangement was of the type used by Trapeznikov (1961). The spring was made of fine quartz fibres drawn from a rod having a diameter of about 13 mm. The length or the number of turns of the spring depended on the diameter of the fibre. Only springs having sensitivity (expansion) of about 10 cm./gm. were chosen for our experiments. The cover slide of the dimensions 51 x 23 x 0.1 mm. was provided with a loop at the top in order to attach it to a hood at the lower end of the spring. The main part of the set up consisted of a glass tube about 45 mm. in diameter and about 250 mm. in length. The lower part of this tube is dipped into water and is little spread out as a damping device for the ripples. The top of the tube is provided with a lid fitted in position by a ground glass joint and a hook for the spring to be attached. The elongation of the spring could directly be read with the help of a pointer attached to it, on graduations impressed on the wall of the glass tube. The working arrangement was to lower the glass tube along with the lid, spring and slide in respective positions, vertically so that the slide just touches the water surface. Now, under the resultant of the three forces acting on the slide e.g. G downwards, buoyancy



upwards and surface tension pull downwards, the slide is pulled inside the water thereby elongating the spring. With the initial elongation known, the elongation due to the pull of the water was determined. The process of touching the slide to the water surface or lifting out of it was done with the help of a moveable clamp. This clamp could be fitted to a bracket at the side wall of the evaporimeter pan and the whole glass tube was held in position. The cover slide could be made to touch the water surface slowly enough without disturbing the film spread on it with the help of the fine threadings of the said clamp. The glass tube prevents disturbance of the spring by wind as well as damps the ripples as it dips inside the water.

The elongation of the spring was calibrated in terms of surface tension with appropriate liquids in the laboratory. A graph of elongation of the spring in various standard pure liquids e.g. water (pure double distilled), nitrobenzene, aniline, benzene, octanol and ethanol was plotted against their respective surface tensions, which varied from 22 dynes/cm. to 72 dynes/cm. and linear curve was obtained. A measured value of the elongation of the spring would enable us therefore to straight away determine the surface tension of the liquid. Thus in the evaporimeters the surface tension of the film covered water surface was determined with the spring elongation and the difference between surface tension of water and surface tension thus

obtained gave the film pressure of the particular film. The purity of the liquids used for calibration was attained by repeated fractional distillation and physical or chemical methods and it was checked in a vapour phase chromatograph. The cover slides were scrupulously chosen to be of the same weight for the validity of the calibration and those slides along with the glass tube were carefully cleaned with hot chromic acid and distilled water before each measurement. A small hole was provided at the top for the adjustment of the pressure of the enclosed air when it was compressed by dipping the glass tube downwards in water.

The disturbance of the monolayer on water surface due to the dipping of the film pressure balance was considered negligible because the area it occupies was small enough as compared to the total surface area of the evaporimeter pans. The film pressure measurements were undertaken simultaneously with evaporation reduction measurements, thereby obtaining day-time and night-time pressure to compare with day and night time reductions.

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## PART - II

### CHAPTER - III

#### RESULTS AND DISCUSSION

Typical results of percent water evaporation reduction efficacies of various film forming materials and their mixtures have been presented in this chapter. Performances of pure  $C_{16}$ -OH,  $C_{18}$ -OH,  $C_{16}$ -OC<sub>2</sub>H<sub>4</sub>OH and  $C_{18}$ -OC<sub>2</sub>H<sub>4</sub>OH and mixtures in various proportions of  $C_{16}$ -OH and  $C_{18}$ -OH,  $C_{16}$ -OC<sub>2</sub>H<sub>4</sub>OH and  $C_{18}$ -OC<sub>2</sub>H<sub>4</sub>OH,  $C_{16}$ -OH and  $C_{16}$ -OC<sub>2</sub>H<sub>4</sub>OH, and  $C_{18}$ -OH and  $C_{18}$ -OC<sub>2</sub>H<sub>4</sub>OH, have been plotted in terms of water evaporation reduction and film pressures in Figures 1-3. The comparative efficiencies of alcohols, alkoxy-ethanols and -propanols of  $C_{16}$ -,  $C_{18}$ - and  $C_{22}$ - carbon chain along with  $C_{16}$  and  $C_{18}$  alkoxy butanols have been reported in Tables-IX and X. Various ethylene oxide condensation products of  $C_{18}$ -OH and  $C_{16}$  +  $C_{18}$ -OH mixtures of different proportions have also been studied to determine the feasibility of such compounds being used as water evaporation retardants. The use of these compounds on a large scale would be economical. Performance data on ethylene oxide condensation products are also presented in Tables-IX and X. Although there were variations in the evaporation results from one experiment to another due to the non-reproducible ambient (atmospheric) conditions.

However, the general trends were found to be the same.

### Durability Test

In Fig. 1a the performances of the pure compounds, namely cetyl alcohol, stearyl alcohol, hexadecoxy ethanol and octadecoxy ethanol have been compared with those of various compositions of cetyl-stearyl alcohols. It may be seen that the cetyl-stearyl alcohol mixtures showed better performances as compared to the component alcohols. Both the natural and synthetic mixtures indicated more or less the same durabilities. If one compares the difference in reduction during the day and night times, natural mixtures invariably displayed larger difference especially on the first day. All the alcohol films deteriorated considerably in two to three days' time.

Hexadecoxy ethanol gave nearly 50 percent reduction on the first day and it was more durable as compared to the alcohols or their mixtures. The film of octadecoxy ethanol exhibited highest efficacy as compared to pure cetyl alcohol, stearyl alcohol, their mixtures and hexadecoxy ethanol. It also showed larger difference in day and night time reductions. The results of hexadecoxy ethanol and octadecoxy ethanol mixtures have been presented in Fig. 1b. It is observed that the reduction during the day was as high as 95 percent for 30:70 and 40:60 natural mixtures. These films were quite durable for about five days and large differences during the day and the night



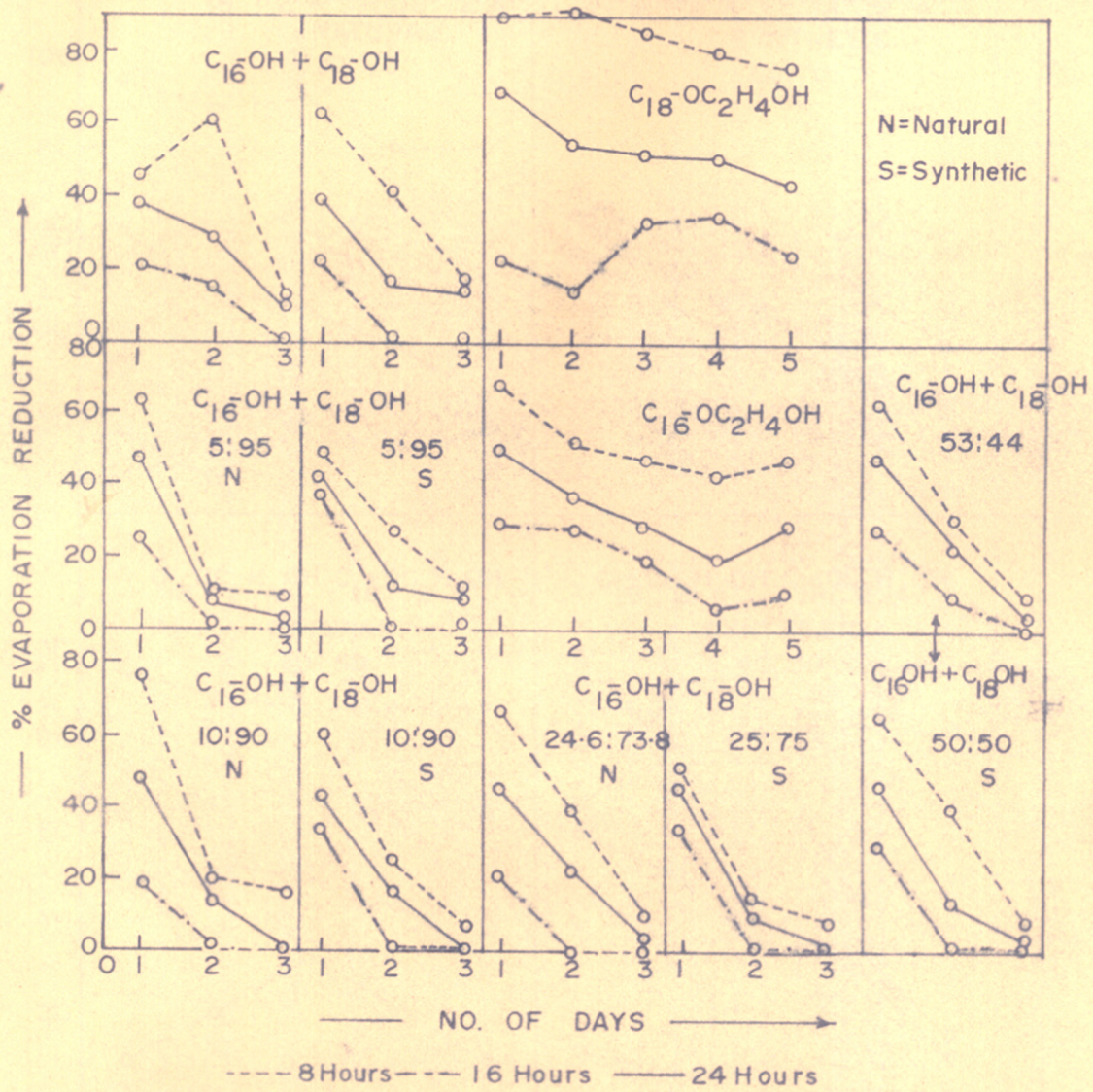


FIG. 1a

DURABILITY TEST

PURE COMPOUNDS AND CETO-STEARYL ALCOHOL, NATURAL & SYNTHETIC MIXTURES



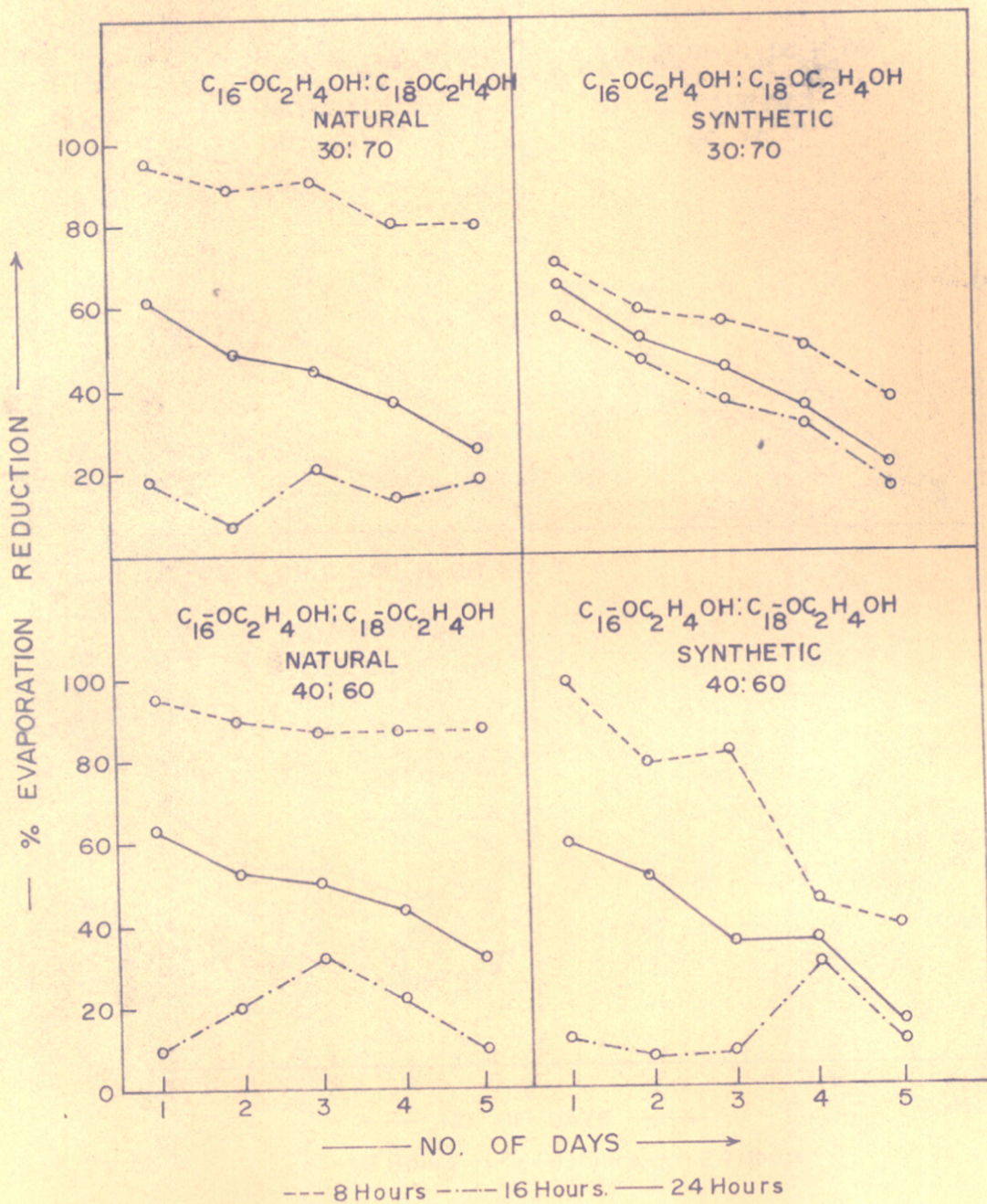


FIG. 1 b

DURABILITY TEST

ALKOXY ETHANOL MIXTURES

$C_{16}-OC_2H_4OH + C_{18}-OC_2H_4OH$  (NATURAL & SYNTHETIC)



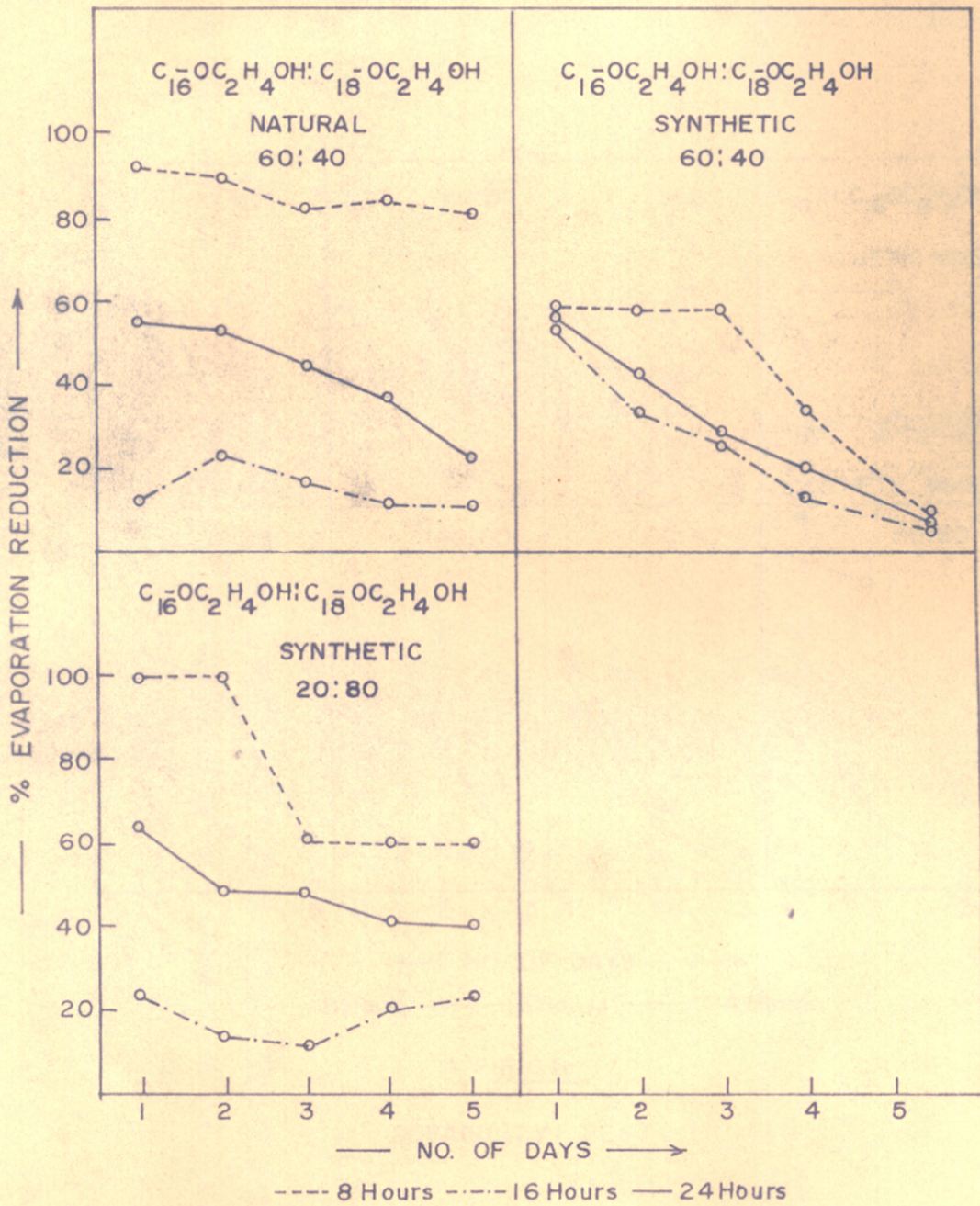


FIG. 1 b (Contd.)



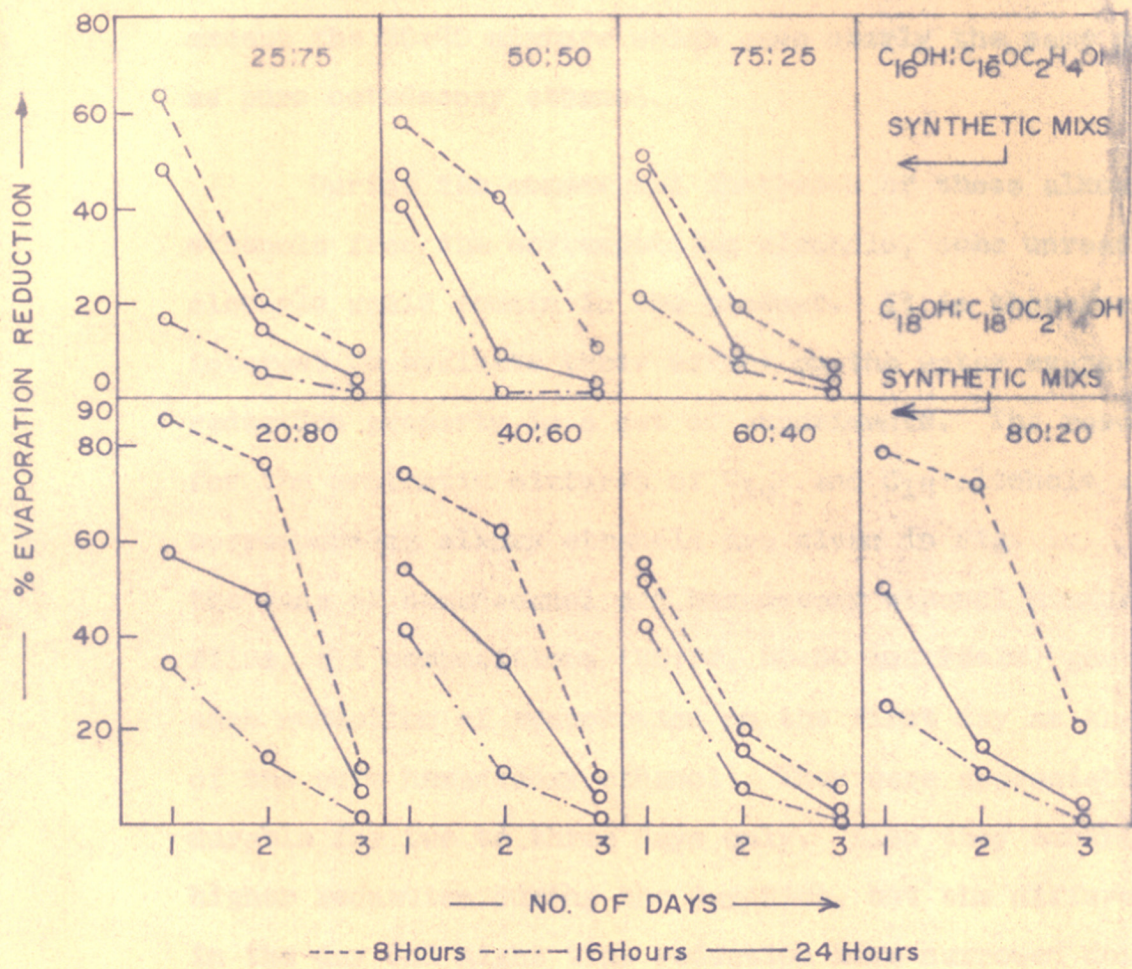


FIG.1c

DURABILITY TEST

SYNTHETIC MIXS. ALCOHOL + ALKOXY ETHANOL



time reductions were observed as compared to synthetic mixtures. All the mixture films showed more or less the same water evaporation reduction as well as durability except the 20:80 mixture which gave nearly the same reduction as pure octadecoxy ethanol.

During the commercial syntheses of these alkoxy ethanols from the corresponding alcohols, some unreacted alcohols would remain in the product. It is therefore of interest to evaluate their effect on the water evaporation reduction property in a set of experiments. The results for the synthetic mixtures of  $C_{16}$ - and  $C_{18}$ -alcohols and corresponding alkoxy ethanols are given in Fig. 1c. In the case of hexadecanol and hexadecoxy ethanol mixture films, all compositions (25:75, 50:50 and 75:25) gave nearly same reduction of evaporation on the first day as that of the pure hexadecoxy ethanol. They were appreciably durable for two to three days only. Also they exhibited higher reduction during the day time, but the differences in the day and night time reduction have narrowed down compared to the alcohol films.

The mixture films of octadecanol and octadecoxy ethanol gave much higher reduction during the day time than the corresponding films of the hexadecanol and hexadecoxy ethanol under same conditions. The reduction for 24 hours' period is about 58 percent on the first day for 20:80 mixture, which is higher than the others and is only about

10 percent less than that of pure octadecyloxy ethanol. The performances of  $C_{16}$ ,  $C_{18}$  and  $C_{22}$  ethanols have been compared with those of  $C_{16}$  alcohol and various mixtures of  $C_{16} + C_{22}$  (25:75, 50:50 and 75:25) and  $C_{18} + C_{22}$  (25:75, 50:50 and 75:25) ethanols in Table-IX A. The effect of one ethanol present into another as an impurity is best known by testing them simultaneously with pure components. At low humidity (about 27%) and high temperature range ( $17^{\circ}$ - $33^{\circ}$ C) with a wind velocity of about 3 miles/hour,  $C_{22}$  ethanol exhibited highest evaporation reduction as compared to other compounds possibly due to its high rate of spreading (more compact nature of the film) and fast healing capacity. Under such typical summer conditions it gave about 63% evaporation reduction on the first day while  $C_{18}$  ethanol gave about 66%. Both the  $C_{18}$  and  $C_{22}$  films remained efficacious till the third day giving about 44% and 51% evaporation reduction respectively while all other films showed negligible reduction on the third day.  $C_{16}$ -alcohol did not stand for more than one day while  $C_{16}$  ethanol stayed for two days for the deterioration of the  $C_{16}$  alcohol film due to evaporation and dissolution was very rapid. On the first day all the mixtures gave evaporation reduction values intermediate between their pure components but deteriorated faster as a result, all of them showed evaporation reduction below 10 percent on the third day except 25:75 mixtures of  $C_{16} + C_{22}$  and  $C_{18} + C_{22}$  ethanols. The mixtures deteriorated fast

TABLE - IX A

Evaporimeter studies on mixtures of C<sub>16</sub> + C<sub>22</sub> and C<sub>18</sub> + C<sub>22</sub> alkoxy ethanols.

Durability Test

No. of days	Weather conditions		Absolute water evaporation in blank pans (litres)	Cetyl alcohol	Percent water evaporation reduction										
	Temp. °C	Humidity %			Wind-velocity Miles per hour	C <sub>16</sub> etha-nol	C <sub>16</sub> + C <sub>22</sub> 50:50	C <sub>22</sub> eth-anol	C <sub>18</sub> eth-anol	C <sub>18</sub> + C <sub>22</sub> 50:50					
1	38	17	25	3.43	14.3	32.9	41.5	65.2	58.2	57.2	66.9	64.1	64.4	65.5	68.3
2	38	18	27	3.03	15.2	5.6	23.3	44.4	41.1	39.2	57.9	51.3	23.6	26.3	55.9
3	39	17	30	2.76	14.1	0	7.1	13.0	8.4	7.5	51.0	44.6	0	2.8	17.2

probably because the major components in the mixture are  $C_{16}$  or  $C_{18}$  ethanols.

In Table-IX B, the performances of pure compounds namely  $C_{16}$ ,  $C_{18}$  and  $C_{22}$  alkoxy propanols along with  $C_{16}$ ,  $C_{18}$  and  $C_{22}$  alcohols, alkoxy ethanols and  $C_{16}$  and  $C_{18}$  butanols were compared. Alkoxy ethanols were found to be generally showing better performance as compared to alcohols, propanols and butanols of corresponding chain-lengths for their better spreadability.  $C_{16}$  alcohol remained efficacious only for first two days, showing little evaporation reduction on the third day.  $C_{18}$  alcohol also gave little evaporation reduction on the third day but it showed higher percent reduction on the first two days as compared to  $C_{16}$  alcohol due to high ambient temperature ( $17^{\circ}$ - $39^{\circ}$ C) at which it has better rate of spreading.  $C_{22}$  alcohol gave a meagre 21 percent reduction on the first day and thereafter showed little or no evaporation reduction, a behaviour which may be attributed to the fact that  $C_{22}$  alcohol has very poor rate of spreading even at the prevailing higher temperatures. Hexadecoxy ethanol gave almost comparable values of evaporation reduction with  $C_{16}$  and  $C_{18}$  alcohol.  $C_{22}$  ethanol was the most efficient water evaporation retardant. It lasted for four days giving as high as 70% evaporation reduction on the first day and about 30% on the fourth day.  $C_{18}$  ethanol lasted for as many number of days, consistently showing a

TABLE - IX B

Evaporimeter studies of alkoxy propanols and alkoxy butanols as compared to alkoxy ethanols and alcohols.

Durability Test

No. of days	Weather conditions			Absolute water evaporation in blank pans (litres)	Percent water evaporation reduction											
	Temp. °C	Humidity	Wind-velocity Miles per hour		ALCOHOLS		ALKOXY ETHANOLS		ALKOXY PROPANOLS		ALKOXY BUTANOLS					
					C16	C18	C16	C18	C16	C18	C16	C18				
1	39	18	45	1.74	12.0	35.1	44.8	23.9	36.9	60.7	65.1	39.8	45.8	53.2	40.0	48.7
2	39	17	37	1.51	10.0	23.0	34.0	0	22.5	55.0	58.0	28.1	38.6	46.7	30.6	39.7
3	39	17	34	1.63	11.9	0	18.8	0	12.9	46.6	51.6	1.6	5.0	26.6	23.1	24.5
4	40	18	30	2.14	12.8	0	0	0	0	12.5	25.3	0	0	0	0	6.1

little lower evaporation reduction than C<sub>22</sub> ethanol. C<sub>22</sub> propanol gave even higher percent evaporation reduction on the first day than C<sub>18</sub> ethanol for its better spreadability but deteriorated on fourth day. C<sub>16</sub> and C<sub>18</sub> butanols gave comparable results with C<sub>16</sub> and C<sub>18</sub> propanols all of them becoming non-efficacious on the fourth day.

Condensation of ethylene oxide with stearyl alcohol and cetyl-stearyl alcohol mixtures to obtain corresponding alkoxy ethanols were tried as it may turn out to be a cheaper process for the preparation of alkoxy ethanols on a large scale. Condensation products obtained for reaction temperatures between 115°-155°C were analysed and found to contain only 15-20 percent of the monocondensates, 60-70 percent unreacted alcohols and 15-25 percent polycondensates. Both distilled and undistilled products were evaluated as water evaporation retardants in the evaporimeter pans the results of which are shown in Table-IX C. 1 mole ethylene oxide condensation products of cetyl-stearyl alcohol was found to be comparable to the corresponding synthetic mixture of alcohol and alkoxy ethanol. Ethylene oxide condensation product of cetyl-stearyl in the molar ratio of 1:0.5 moles showed better evaporation retardation properties as compared to the other condensation products probably due to the maximum conversion to mono-condensate. Undistilled products of the same gave consistently lower evaporation reduction. All the condensation products showed evaporation reduction values intermediate between those of alcohols and alkoxy ethanols.

TABLE - IX C

Evaporimeter studies of ethylene oxide condensation products

Durability Test

No. of days	Weather conditions		Blank pans (absolute water evaporation) Litres	Percent water evaporation reduction													
	Temp. °C	Wind velocity Miles per hour		Humidity %	Cetyl: Stearyl alcohol mixture 25:75		Cetyl: Stearyl Alcohol		Ethylene oxide condensation products		Syntetic mixture C18 ethan-ol						
					Cetyl: Stearyl Alcohol	Undis-tilled	Dis-tilled	STEARYL ALCOHOL	Undis-tilled	Dis-tilled		STEARYL ALCOHOL	Undis-tilled	Dis-tilled			
1	38	18	1.03	37	12.0	37.5	51.0	55.5	50.0	48.5	41.9	51.0	46.0	50.0	37.0	51.0	60.0
2	37	18	1.29	38	10.8	28.0	36.2	48.4	33.8	40.8	23.5	35.5	29.4	32.2	18.9	35.1	57.1
3	38	18	1.55	40	13.4	7.2	16.9	27.2	15.2	20.2	10.3	18.3	16.4	12.8	8.1	19.6	48.2
4	39	17	1.43	42	12.7	0	0	12.7	0	9.6	0	8.5	0	0	0	6.2	40.0

### Everyday Replenishment

The evaporation reduction by the monolayers of the above mentioned compounds and their mixtures have been studied by replenishing the films every day through fresh additions. In Fig. 2a are given the representative results for cetyl and stearyl alcohols and their mixtures and also for pure hexadecoxy and octadecoxy ethanols. The 25:75 natural cetyl-stearyl alcohol mixture films gave 60 percent reduction on the first day which was maintained for three days and deteriorated thereafter due to progressive contamination of the film with deleterious impurities. Under the ambient conditions it was the best of all alcohol compositions, both synthetic and natural. However, the film of this mixture deteriorated rapidly if it was not replenished every day as indicated earlier. It was found that octadecoxy ethanol gave a steady value of about 60 percent for five days which otherwise would have fallen down to about 40 percent or so. The differences in day and night time evaporation reductions had been narrowed down by 10-15 percent, compared to the results obtained during durability tests for the same compounds. Cetyl-stearyl alcohol mixtures when replenished every day maintained better performance than pure cetyl and stearyl alcohols and hexadecoxy ethanol, possibly due to the presence of some unknown impurities in the hydrogenolysis products, which facilitate better spreading or healing of the film.



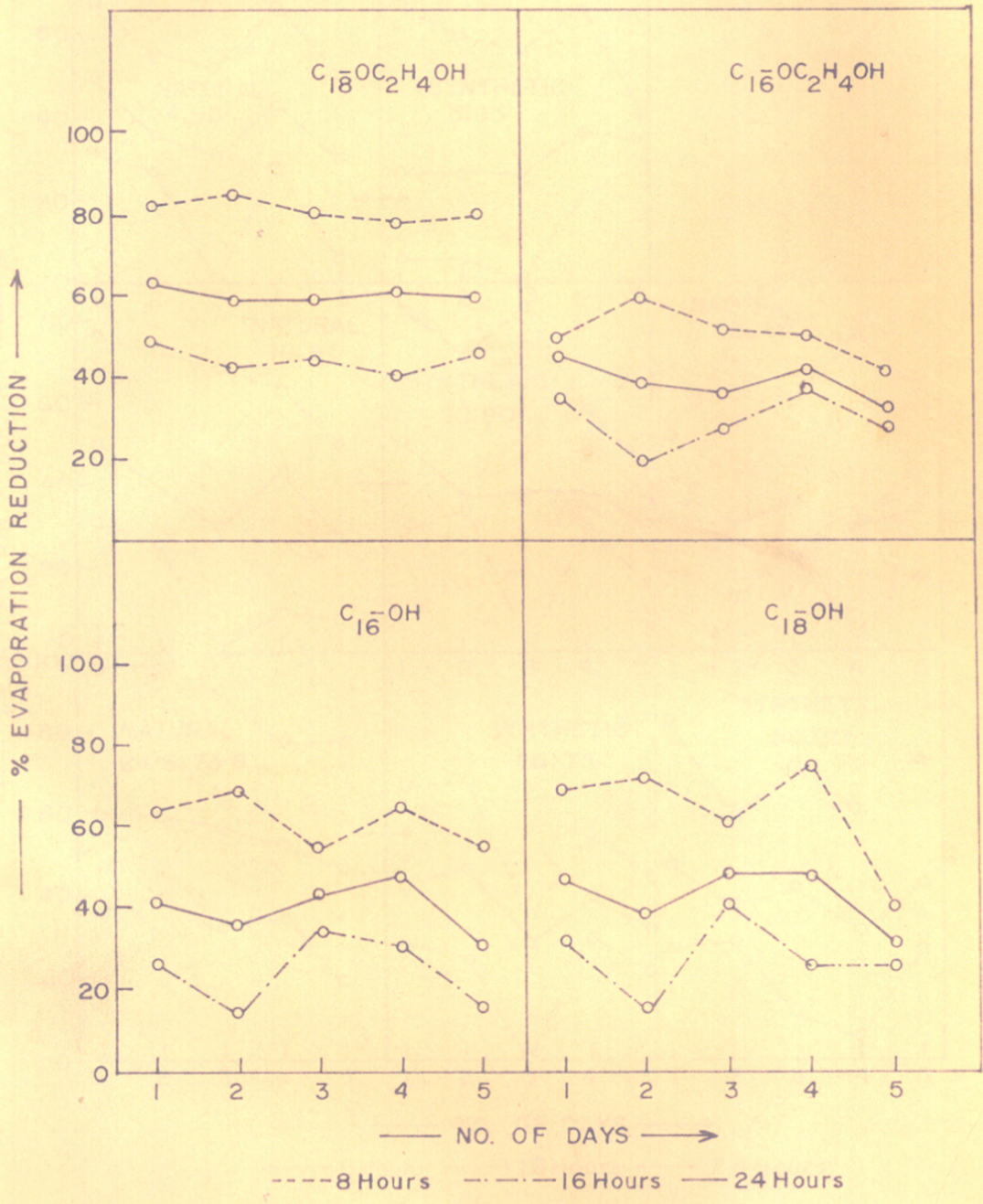


FIG. 2a

EVERYDAY REPLENISHMENT, PURE COMPOUNDS



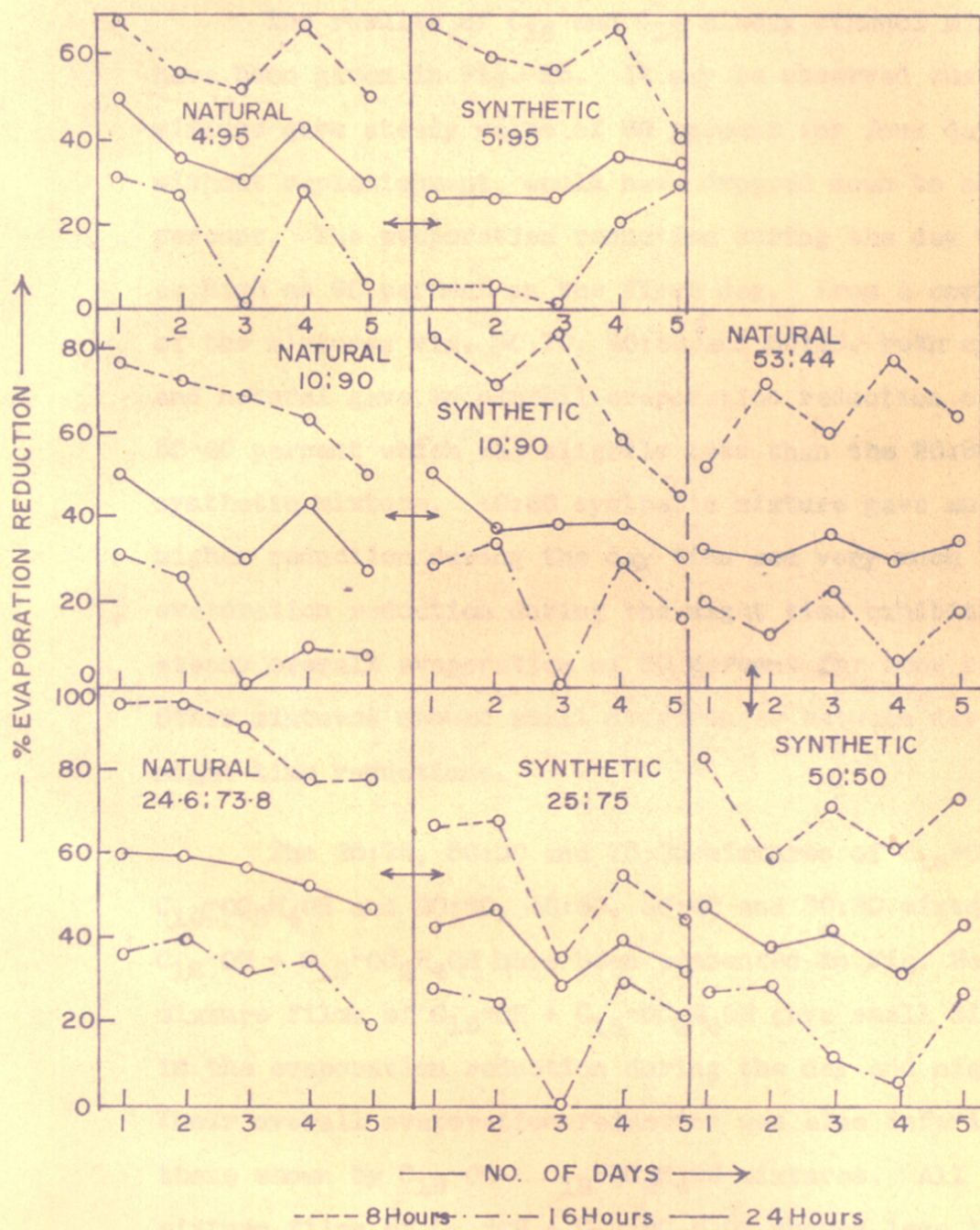


FIG. 2a (Contd.)

EVERYDAY REPLENISHMENT CETO STERYL MIXTURES  $C_{16}OH:C_{18}OH$

The results of  $C_{16}$  and  $C_{18}$  alkoxy ethanol mixtures have been given in Fig. 2b. It may be observed that 20:80 mixture gave steady value of 60 percent for four days which, without replenishment, would have dropped down to about 45 percent. The evaporation reduction during the day time was as high as 90 percent on the first day. From a comparison of the mixtures viz. 30:70, 40:60 and 60:40, both synthetic and natural gave an overall evaporation reduction of about 50-60 percent which was slightly less than the 20:80 synthetic mixture. 40:60 synthetic mixture gave much higher reduction during the day time and very much lower evaporation reduction during the night time exhibiting a steady overall evaporation of 50 percent for four days. Other mixtures showed small differences between day and night time reductions.

The 25:75, 50:50 and 75:25 mixtures of  $C_{16}$ -OH +  $C_{16}$ -OC<sub>2</sub>H<sub>4</sub>OH and 20:80, 40:60, 60:40 and 80:20 mixtures of  $C_{18}$ -OH +  $C_{18}$ -OC<sub>2</sub>H<sub>4</sub>OH have been presented in Fig. 2c. The mixture films of  $C_{16}$ -OH +  $C_{16}$ -OC<sub>2</sub>H<sub>4</sub>OH gave small difference in the evaporation reduction during the day and night times. Their overall evaporation reduction was also inferior to those shown by  $C_{18}$ -OH +  $C_{18}$ -OC<sub>2</sub>H<sub>4</sub>OH mixtures. All the mixture films of  $C_{16}$ -OH +  $C_{16}$ -OC<sub>2</sub>H<sub>4</sub>OH showed less than 40 percent reduction for 24 hours which remained steady for five days. The behaviour of these mixtures was nearly same as that of pure cetyl and stearyl alcohols. The 20:80 mixture of  $C_{18}$ -OH +  $C_{18}$ -OC<sub>2</sub>H<sub>4</sub>OH gave almost the same



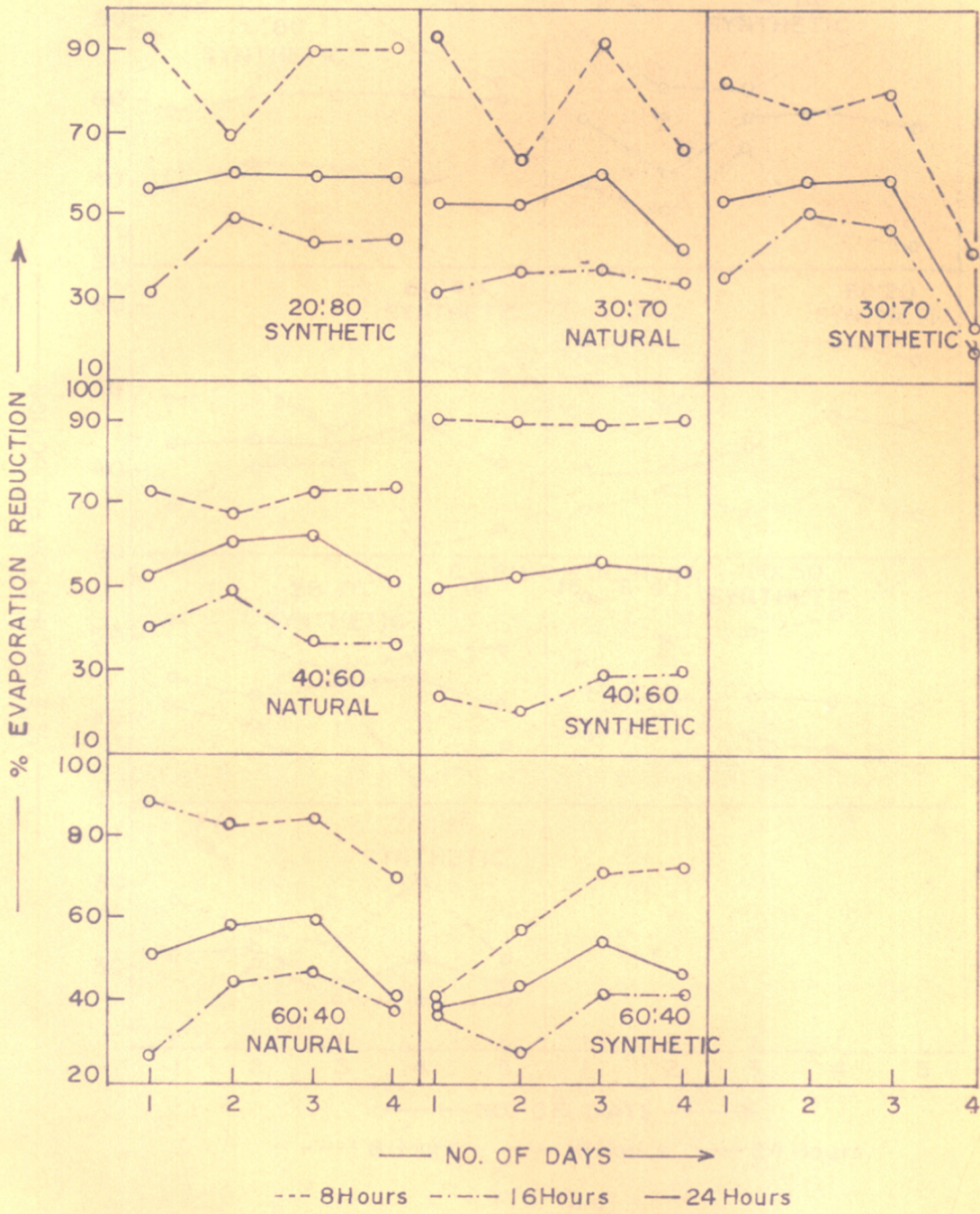


FIG. 2 5

EVERYDAY REPLENISHMENT, ALKOXY ETHANOL MIXTURES  $C_{16}$ : $C_{18}$



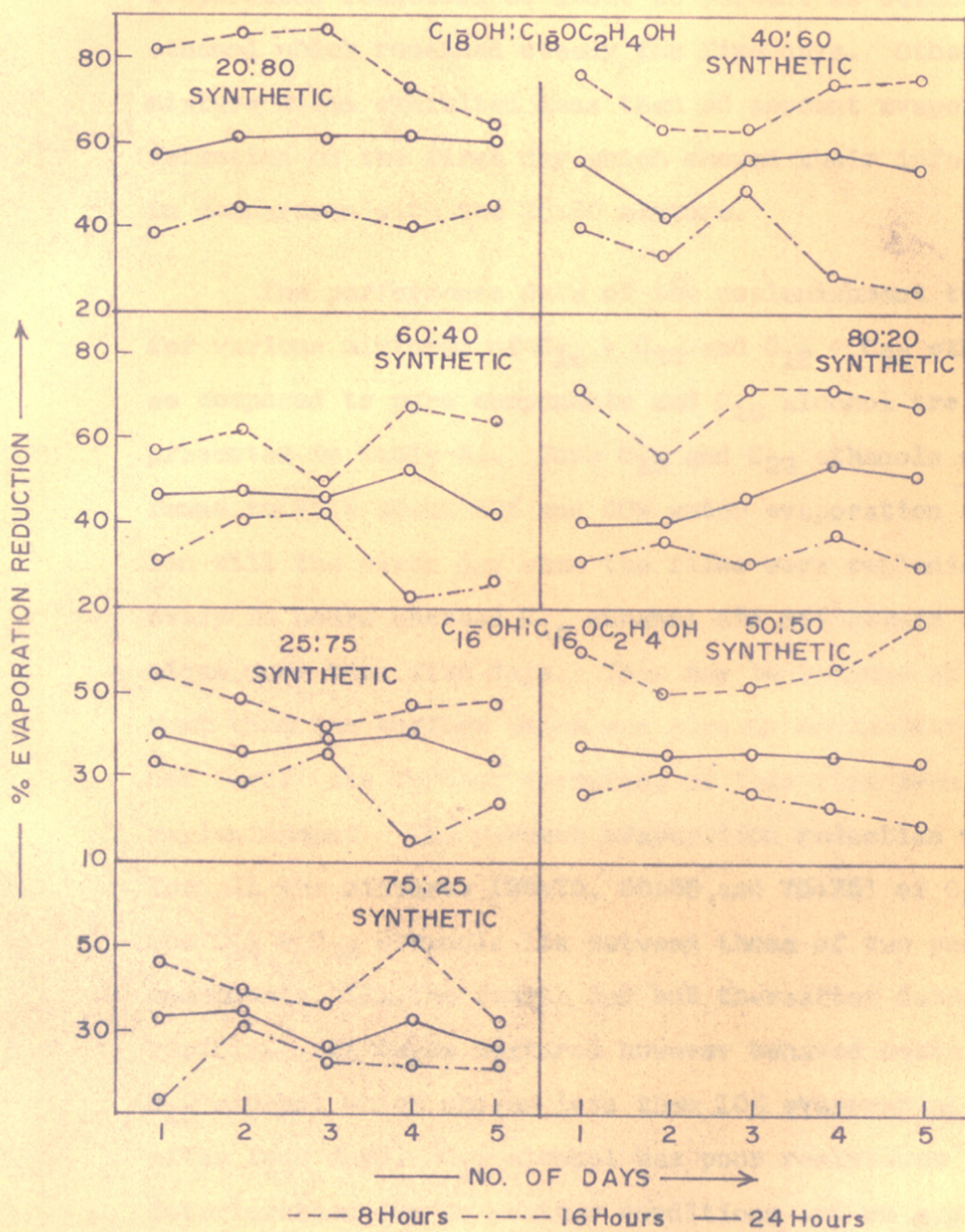


FIG. 2c

EVERYDAY REPLENISHMENT, ALCOHOL:ETHANOL MIXTURES

evaporation reduction of about 60 percent as octadecoxy ethanol which remained steady for five days. Other mixture films exhibited less than 50 percent evaporation reduction on the first day which showed their inferiority in comparison with the 20:80 mixture.

The performance data of the replenishment test for various mixtures of  $C_{16} + C_{22}$  and  $C_{18} + C_{22}$  ethanols as compared to pure components and  $C_{16}$  alcohol are presented in Table-XA. Pure  $C_{18}$  and  $C_{22}$  ethanols were found to give about 40% and 50% water evaporation reduction till the sixth day when the films were replenished every 24 hours whereas  $C_{16}$  ethanol did not remain efficacious more than five days. This may be because of the fact that the surface which was already contaminated, does not facilitate further spreading of this film even on replenishment. The percent evaporation reduction values for all the mixtures (25:75, 50:50 and 75:25) of  $C_{16} + C_{22}$  and  $C_{18} + C_{22}$  ethanols lie between those of two pure components till the fourth day but thereafter deteriorates rapidly. All these mixtures however behaved better than  $C_{16}$  alcohol which showed less than 10% evaporation reduction after four days.  $C_{16}$  alcohol has poor resistance to deterioration due to weather conditions and no appreciable resealing capacity thus having no effect of replenishment after four days.

Table-XB presents the performances of pure alcohols, alkoxy ethanols, propanols and butanols when the films were

TABLE - X A

Evaporimeter studies on mixtures of  
C16 + C22 and C18 + C22 alkoxy ethanols.  
Everyday Replenishment Test

No. of days	Weather conditions		Absolute water evaporation in blank pans (litres)	Percent water evaporation reduction											
	Temp. °C	Humidity %		Wind-velocity Miles per hour	Cetyl alcohol	C16 ethanol	C19 + C22		C22 ethanol	C18 ethanol	C18 + C22				
							25:75	50:50				75:25			
1	39	18	56	2.35	13.3	35.9	40.0	63.2	61.7	43.9	69.2	60.2	65.6	65.6	61.2
2	37	18	56	3.75	12.2	23.4	23.6	57.6	52.7	46.7	68.0	59.0	65.3	61.6	59.9
3	33	17	54	3.43	12.0	25.8	23.2	54.5	51.7	45.0	66.8	59.3	63.9	61.4	57.8
4	37.5	18	55	2.91	13.1	22.6	27.8	49.0	45.2	31.8	58.0	53.4	56.9	54.6	51.5
5	37	17	56	3.25	13.4	6.7	16.4	34.4	17.6	16.2	48.8	42.2	44.8	40.7	37.4
6	39	17	56	2.13	12.2	0	15.3	26.1	15.9	14.7	43.3	40.0	45.7	23.2	16.8



TABLE - X B

Evaporimeter studies of alkoxy propanols and alkoxy butanols as compared to alkoxy ethanols and alcohols.

Everyday Replenishment Test

No. of days	Weather conditions			Absolute water evaporation in blank pans (litres)	Percent water evaporation reduction										
	Temp. °C	Humi- dity %	Wind- velo- city Miles per hour		ALCOHOLS		ALKOXY ETHANOLS		ALKOXY PROPANOLS		ALKOXY BUTANOLS				
Mx	Mn			C16	C18	C22	C16	C18	C22	C16	C18	C22	C16	C18	
1	36	18	35	1.60	26.9	40.6	19.7	33.3	57.8	65.0	38.6	50.5	57.1	34.4	52.7
2	38	17	23	1.68	29.0	41.4	0	30.0	56.4	63.2	33.0	42.5	60.2	37.1	45.7
3	38	17	22	2.48	25.2	40.4	0	34.8	55.5	62.9	32.3	43.9	55.5	33.3	36.8
4	38	17	28	3.10	20.8	33.8	0	31.5	55.8	61.1	31.3	51.1	58.0	36.0	37.0
5	37	17	26	2.13	20.0	33.5	0	35.2	48.5	55.5	31.7	43.5	52.8	28.8	36.2
6	38	18	32	2.51	0	8.7	0	15.6	45.4	51.1	23.3	40.0	48.1	8.3	35.1



replenished every day. The percent evaporation reduction shown by the various films were similar on the first day as shown in the case of durability test but remained efficacious for more than five days.

C<sub>22</sub> ethanol gave the maximum evaporation reduction on the first day (about 65%) with C<sub>18</sub> ethanol and C<sub>22</sub> propanol giving about same (57%) reduction. All these films remained efficacious till the sixth day giving about 45-50 percent evaporation reduction each. C<sub>16</sub> and C<sub>18</sub> butanols gave consistently lower percent evaporation reduction than the corresponding propanols and ethanols but maintained the efficacy for about six days. This showed their resistance to the deterioration but less spreadability.

C<sub>16</sub> and C<sub>18</sub> alcohols gave usual values of evaporation reduction as observed earlier but C<sub>22</sub> alcohol did not give appreciable reduction even on the 2nd day in spite of replenishment. This peculiar behaviour of C<sub>22</sub> alcohol may be due to the fact that it had a very low rate of spreading, more so on contaminated surfaces.

The ethylene oxide condensation products also maintained sufficient efficacy for about six days when replenished every day. From Table-XC it is once again clearly observed that ethylene oxide condensate of 1:0.5 mole cetyl-stearyl was the best compositions as regards water evaporation reduction when compared with other

TABLE - X C

Evaporimeter studies of ethylene oxide condensation products

Everyday Replenishment Test

No. of days	Weather conditions		Blank pans (absolute water evaporation) litres	Cetyl: Stearyl alcohol mixture 25:75	Ethylene oxide condensation products			Percent water evaporation reduction	Syntetic ethyl alcohol mixture								
	Temp. °C	Wind velocity Miles per hour			Cetyl: Stearyl Alcohol	STEARYL ALCOHOL	ALCOHOL										
1	38	16	2.37	55	12.3	38.5	42.9	51.3	46.3	45.0	41.5	48.7	45.4	37.2	35.7	43.4	60.0
2	38	17	2.77	62	13.2	30.0	52.7	54.2	48.6	47.9	34.5	48.4	44.8	46.2	29.6	50.9	60.0
3	37	18	1.30	42	12.72	33.9	46.7	52.8	49.1	45.7	40.6	53.0	50.2	45.5	32.4	43.4	57.5
4	38	17	2.05	44	13.2	28.1	47.6	50.2	46.6	43.3	38.0	46.5	40.5	42.4	29.3	43.5	58.5
5	39	19	1.38	42	14.4	29.2	45.0	50.4	46.6	47.3	43.1	43.4	40.5	41.8	32.2	42.1	55.8
6	39	18	1.43	48	13.4	7.6	28.5	40.2	34.4	18.5	4.4	21.8	18.2	18.2	4.1	26.3	47.8

condensates and gave about 40 percent evaporation reduction on sixth day while  $C_{18}$  ethanol showed a higher value of 48 percent on that day. Undistilled condensates consistently gave lower percent evaporation reduction than the distilled ones till the sixth day probably due to the presence of polycondensates. The values of percent evaporation reduction of all the ethylene oxide condensates lied between those of  $C_{18}$  alcohol and  $C_{18}$  alkoxy ethanols. This trend was observed in the case of durability test also.

#### Film Pressure Measurements

It has been shown by Deo (1964) and La Mer (1962) that the evaporation loss is, among others, largely dependent on the film pressure. In view of the large difference in day and night time reductions shown by various monolayers, it is thought desirable to check their film pressures during those periods. Film pressures were therefore, measured for a few selected films and the results have been represented in Figs. 3a and 3b. In Fig.3a are given the film pressures for the day and night hours along with percent evaporation reduction of cetyl and stearyl alcohols, hexadecoxy and octadecoxy ethanols and 50:50 binary mixtures of all these compounds. It was indeed seen that in the day time film pressure was much higher than that in the night time, which was in accordance with the water evaporation reduction results. For example, in an experiment it was observed that the day time film pressure for octadecoxy ethanol was 48 dynes/cm. and the night time pressure

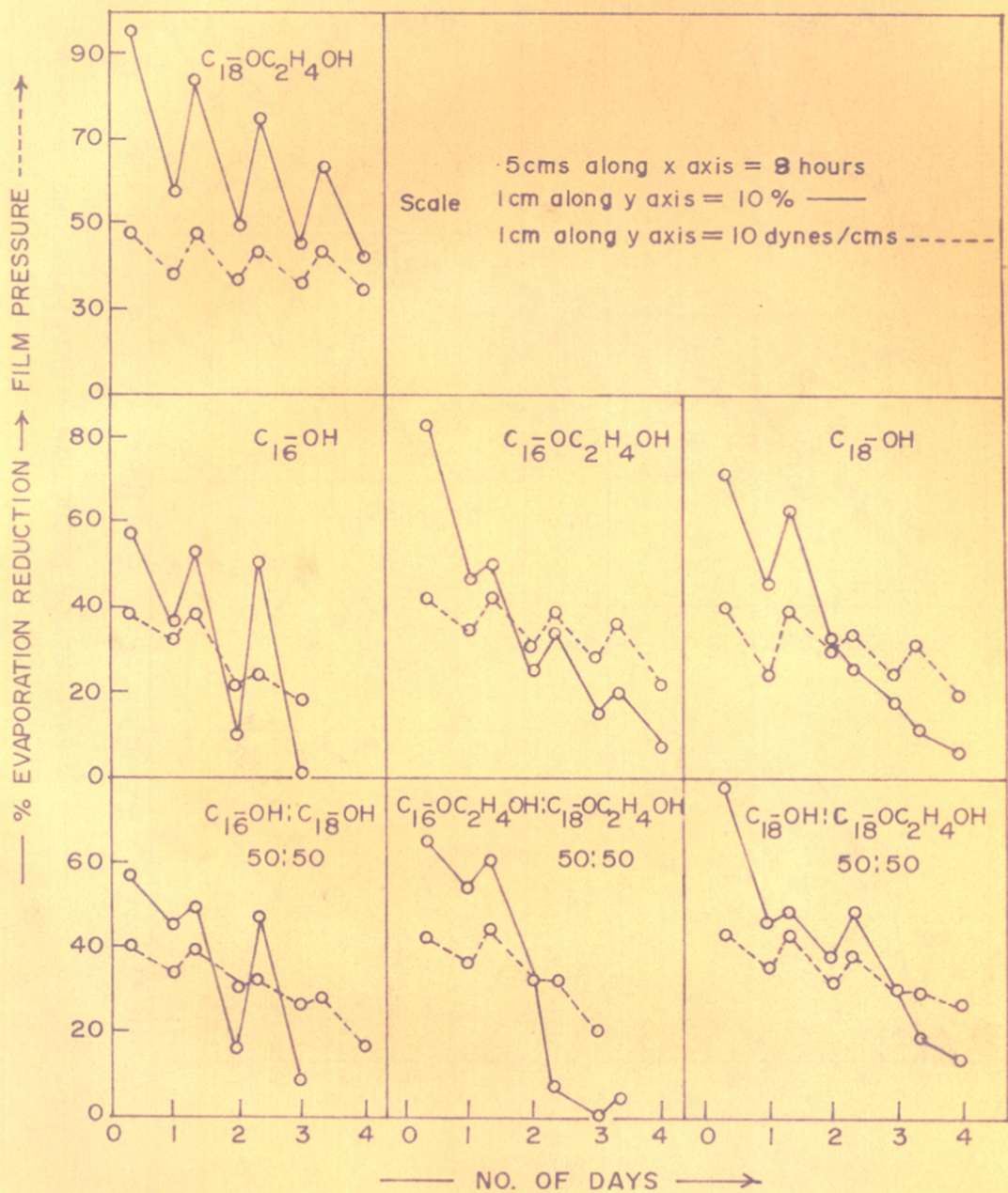


FIG. 3a

FILM PRESSURES  
 DURABILITY TEST



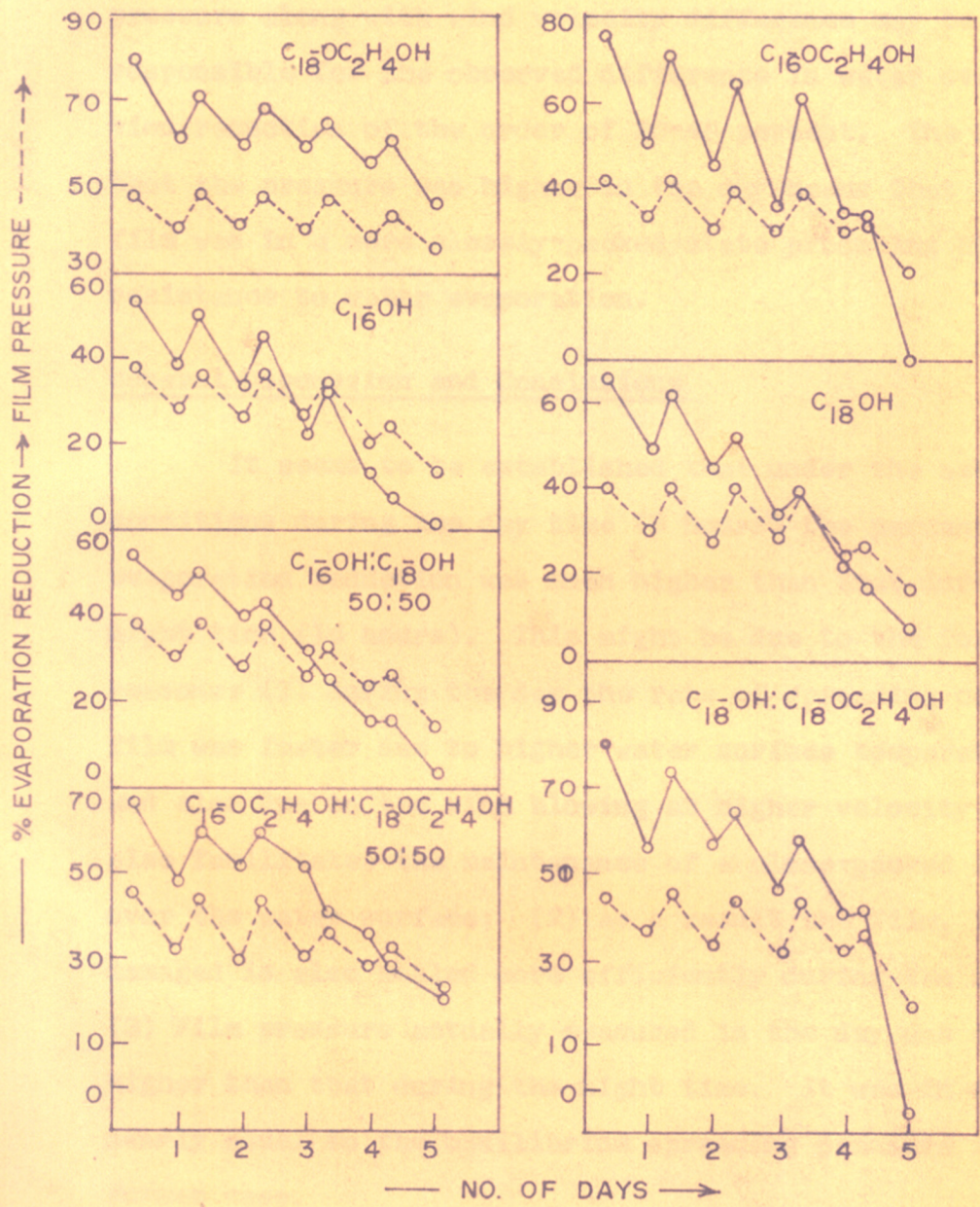


FIG. 3 b

FILM PRESSURES

EVERYDAY REPLENISHMENT TEST

was only 38 dynes/cm. This difference of about 10 dynes/cm. pressure along with wind velocity difference may be mainly responsible for the observed difference in water evaporation reduction of the order of 20-40 percent. The fact that the pressure was higher in the day means that the film was in a more closely-packed state producing higher resistance to water evaporation.

#### General Discussion and Conclusions

It seems to be established that under the ambient conditions during the day time (8 hours) the percent water evaporation reduction was much higher than that during the night time (16 hours). This might be due to the following reasons: (1) During the day the rate of spreading of the film was faster due to higher water surface temperature and also due to the wind blowing at higher velocity, which also facilitates the maintenance of a close-packed film over the water surface; (2) As a result the film, if damaged is also healed more efficiently during the day; (3) Film pressure actually measured in the day was much higher than that during the night time. It was in fact nearly equal to the equilibrium spreading pressure in the former case.

Due to the lower ambient temperature and lower wind velocity prevailing during the night, the film will spread less efficiently to result in lower film pressure and percent reduction of water evaporation.

Amongst the compositions studied under the stated ambient conditions, the film of octadecoxy ethanol was found to be the best water evaporation retardant as it exhibited better spreading property as well as high equilibrium spreading pressure (1964). Although at the high temperature range and low humidities, C<sub>22</sub> ethanol gave higher evaporation reduction, on an overall basis C<sub>18</sub> ethanol seems to be more effective. C<sub>22</sub> propanol also gave comparable results to that of C<sub>18</sub> ethanol under similar conditions, but availability of C<sub>22</sub> alcohol being rather scarce prevents one from considering the practical utility of any derivative of this alcohol i.e. ethanols, propanols or butanols as evaporation retardant. The behaviour of the 20:80 mixture of C<sub>18</sub>-OH + C<sub>18</sub>-OC<sub>2</sub>H<sub>4</sub>OH was nearly same as that of pure C<sub>18</sub> ethanol. The same was true for the 20:80 mixture of C<sub>16</sub>:C<sub>18</sub> ethanol. Thus the presence of as much as 20 percent of C<sub>18</sub> alcohol or C<sub>16</sub> ethanol in C<sub>18</sub> ethanol did not appear to affect its film efficacies appreciably. The 25:75 cetyl-stearyl alcohol natural mixture obtained from cottonseed oil behaves as better water evaporation retardant than synthetic mixtures and pure cetyl and stearyl alcohols. The small amount of unknown but desirable impurities present in the former has been responsible for the better spreadability and hence evaporation reduction. C<sub>18</sub> + C<sub>22</sub> ethanol mixture gave comparative results with both C<sub>18</sub> and C<sub>22</sub> pure ethanols as both of these ethanols show high rate of spreading but deteriorate soon because the two components may have

similar healing property. Ethylene oxide condensation product of 1:0.5 mole of cetyl-stearyl alcohol gave better performance as water evaporation retardant consistently as compared to  $C_{18}$  ethanol which gave about 10 percent more in the evaporation reduction value. Its maintenance and better spreadability may be due to its conversion to monocondensate amongst unreacted alcohol. The salient points can now be therefore summarised in the following:

- I. Alkoxy ethanols are better water evaporation retardant as compared to alcohols. In alkoxy ethanols, polar groups are extended as a result it exhibits stronger adhesion to the subphase water and resistance to evaporation.
- II. The number of  $-CH_2$  group was increased in the polar end to study its effect on water evaporation resistance. Results of propanols and butanols however did not show much improvement over ethanols. At higher ambient temperatures  $C_{22}$  propanol did give comparable values to that of  $C_{18}$  ethanol.
- III. In order to develop a cheaper process for the preparation of alkoxy ethanols on a large scale, ethylene oxide condensation with alcohols and their mixtures were tried. The product of cetyl-stearyl condensation in the molar ratio of 1:0.5 moles showed better water evaporation resistance as compared to other condensation products and pure alcohols.



Study on the various physical properties of all these sets of compounds are underway in this laboratory for further correlation and elucidation of their water evaporation resistance property.

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