SUMMARY

In recent years, considerable attention has been given in controlling the evaporation loss of water stored in lakes and reservoirs, by spreading insoluble monolayers of n-long chain alcohols (C_n-OH, with n= 16, 18, 20 and 22). The corresponding alkoxy ethanols (C_n-OCH_2CH_2OH) have been reported to be superior to the alcohols. With a view to elucidate the behaviour of these compounds in the monolayer state, properties of these are being studied, using several physical chemical techniques.

A study of the surface potential of their monolayers on water surface has been made and the results are described in Part I of the thesis. The monolayer properties, such as rate of spreading and equilibrium spreading pressure, are much influenced by the physical state (crystalline modification) of these compounds which are known to exist in various polymorphic modifications. These compounds have therefore been investigated using the differential thermal analysis technique and the results are reported in Part II of the thesis.

The measurements of surface potential (ΔV) were carried out using the ionizing electrode method. The surface dipole moment (μ_1) has been calculated using the Helmholtz equation $\Delta V = 4\pi n \mu_1$, where n is the concentration of the film-forming molecules per sq. cm. The surface pressure (π) and area per molecule (A) have been determined in a Langmuir trough fitted with horizontal film pressure balance.

The results have been represented in the form of ΔV-π,

ΔV-A, μ_1-A and π-A isotherms obtained at three temperatures (around 15°, 20° and 25°C). All these isotherms show breaks which correspond to two-dimensional phase transitions, such as gas→liquid condensed (G→L_c), liquid condensed→liquid solid or solid (L_c→LS or S) states, similar to those usually observed in the π-A isotherms.

The ΔV often showed nonsteady values above a certain value of A(corresponding to the liquid expanded state) and this has been ascribed to formation of transient patches or nonhomogeneous films.

At pressures above the L_c state, the ΔV rises linearly and rapidly till the LS or S state is attained, after which the change is rather small. The A values corresponding to the breaks in the various isotherms compare very well with each other and also with the literature values of the π-A isotherms.

It is found that the ΔV and μ_1 values for the alkoxy ethanols have nearly 1.5 times higher than those of the alcohols, obviously due to the presence of the more polar and extended oxyethanol group in the former series of compounds. Also, the total change in ΔV or μ_1 for a change in π from 1 dyne/cm to 45 dynes/cm., is much more in the former case due to the much larger value of the resultant intrinsic dipole moment $\bar{\mu}$ or μ_1 and their change with orientation.

As the chain length increases from C_{16} to C_{22}, ΔV or μ_1 also increases in both series of compounds, as also the L_c→LS or S transition pressure. The A values obtained by extrapolation to zero compression of the S region are nearly the same for the alcohols and alkoxy ethanols, but the latter in general shows a more expanded type of film. This is due to

the stronger repulsive forces operating between the extended
polar end group in comparison with the van der Waal's attrac-
tive force operating between the hydrocarbon chains of two
adjacent molecules.

The mixed monolayers of alcohols and alkoxy ethanols
have also been studied to view to investigate the effect of
molecules of different lengths and polarity on the intermolecular
interactions and the packing characteristics in the mixed mono-
layer state. All the mixtures were found to be homogeneous and
the simple mixture law, however, was not found to be applicable
to them. The mixtures like C_{16}-OH + C_{16}-OCH$_2$CH$_2$OH were found to
give ΔV, Δu_1 and $L_c \rightarrow LS$ or S transition pressure values which
are nearly the average of those obtained for the pure components.
But those mixtures where the chain length and the polar group
of the compounds were much different, the ΔV, Δu_1 and $L_c \rightarrow LS$ or
S pressures were appreciably lower than the average values
indicating stronger intermolecular interactions.

The DTA analysis of the alcohols, alkoxy ethanols and
their mixtures have been done in a manually operated apparatus
fabricated in our laboratory. The heat evolved and absorbed
during phase transformation have been computed from the area
under the peak. In general, two peaks, one due to phase transi-
tion in the solid state a few degrees below the fusion, and the
other corresponding to the fusion (melting) of the compound,
were observed. The transition and fusion temperatures go on
increasing as the chain length increases in both the series.
Similarly, the heat of fusion ΔH_f also increases with the chain
length. The alkoxy ethanols have lower transition and fusion

temperature than the alcohols. The entropy change during fusion is nearly 2-3 times more than that during solid state transitions, obviously due to much more disorder taking place in the system during the fusion process.

The DTA of the mixtures (alcohol + alcohol, alkoxy ethanol + alkoxy ethanol, and alcohol + alkoxy ethanol) in various molecular proportions have been studied and the data have been analysed and also discussed. These were found to form homogeneous solid solutions.

The hydrates of C_{16}-OH, C_{18}-OH and C_{20}-OH have been studied by the differential calorimetric method. In the presence of water, the transition temperature is lowered and the melting point is increased significantly. It appears that a hydrate of definite composition with the proportion of water:alcohol as 1:3 can be identified and the possible hydrogen bonded structure is suggested.