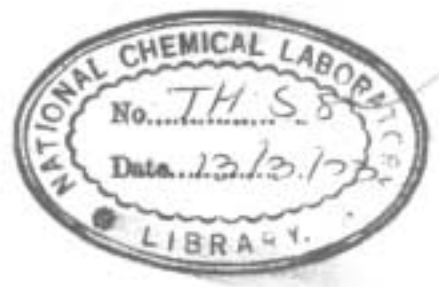


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**THE DIELECTRIC PROPERTIES
OF n-LONE CHAIN ALCOHOLS
AND THEIR DERIVATIVES**

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A THESIS

Submitted **To The**

University of Bombay

for

THE DEGREE OF MASTER OF SCIENCE

(In Physical Chemistry)

by

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The dielectric properties of a series of n-length chain alcohols C_n -CH (n=10,12,14,16,18,20,22), n-alkoxy ethanols C_n -CC₂H₄OH (n=16,18,20,22) and n-alkoxy propanols C_n -OC₃H₆OH (n= 16,18,20,22) have been studied at different temperature and frequencies.

All the compounds except C_{10} -CH and C_{12} -OH are studied both in liquid and solid states to investigate the molecular rotation and the phase transition in the solid state.

In the cooling process the alcohols from C_{14} to C_{22} showed a rotating α phase below the freezing point. The rotating phase existed over a range of temperature from about 2°C to 5.4°C depending on the chain length. The rotating phase is also observed in the warming experiments even after holding the sample in non-rotating phase for a long period (fifteen hours). In these experiments the transition occurred very near the respective melting points of C_{14} , C_{16} , and C_{18} alcohols and the rotating phase is not stable over any temperature range. The C_{20} and C_{22} alcohols exhibited the rotating phase over a range of about 1.5°C.

The transition temperatures are higher than those observed by Smyth et al. which may be attributed to the

higher parity of the compounds used in the present studies.

the alkoxy ethanols exhibit the rotating α phase over a range of temperature of about 11°C to 22°C depending on the chain length a small dispersion is observed in the non-rotating phase which is attributed to the orientational freedom of the polar group

the rotating phase is also observed in the warming experiment the transition is much sluggish compared to that in the alcohols except C₁₆-alkoxy ethanols all the compounds in this series showed the rotating phase for a range of temperature the C₂₀-alkoxy ethanol was held in non-rotating phase for about fifteen hours even then the transition to rotating phase is observed thus indicating that the prolonged holding of the sample in non-rotating phase does not affect the transition to rotating phase

the alkoxy propanols showed a slightly different behaviour than those of previous two series the C₁₆-alkoxy propanol showed the orientational freedom in solid state but solid-solid transition is not observed and hence it is suggested that this compound does not exhibit the rotating phase and the orientational freedom is limited to polar group that this compound does not exhibit the rotating phase and the orientational freedom is limited to polar group only the other three compounds in the series exhibit the rotating phase over a range of temperature from 7°C to 10°C depending on the chain length a large dispersion is observed even after the transition to non-rotating phase and the possibility of segmental rotation is suggested.

in warming experiments the dielectric constant showed a continuous increase with temperature but transition to rotating phase is not observed it is therefore concluded that after the transition to non-rotating phase the compound transfers to a stable state form which the transition to rotating phase is not possible

it is thus observed in the present studies that the change in polar group from hydroxyl to ether group and the extension of the polar group affect the phase modifications the dipole moments of the above mentioned compounds are calculated by Onsager equation

the dipole moments of the alcohols are higher than the vapour state value (~1.66D) at all the temperatures studies the Kirkwood 's'g' factor is calculated at different temperatures and its variation with temperature and chain length is discussed the decrease in 'g' with temperature is attributed to the unassociation of the polymer while the decrease in 'g' with increase in chain length is due to the decrease in degree of association the decrease in the (smaller) temperature dependence of 'g' with the increase in chain length is attributed to the increase in van der Waal forces of attraction and increase in the energy for unassociation with increase in the chain length the rate of decrease of 'g' is accelerated at higher temperature which is attributed to the decrease in the energy for hydrogen bond breaking due to the increase in the proportion of the monomeric molecules.

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the dipole moment of the alkoxy ethanols is almost independent of temperature and chain length and is about 2.19D the theoretical dipole moments for the trans and gauche molecules are calculated the dipole moment calculated for gauche molecule (2.20D) is in good agreement with the experimental value and hence the gauche structure is suggested as one of the possibilities of monomeric molecules in the liquid state

the dipole moment of alkoxy propanols is also almost independent of temperature and the chain length and is about 2.38D. it is suggested that the association is limited to dimeric state only and the temperature range studied the theoretical dipole moments of gauche ring and trans structures are calculated and it is observed that the dipole moment calculated for trans structure (2.36D) is in good agreement with the experimentally observed value (2.38 D) and hence the trans structure is suggested to the monomeric molecules in the liquid state.