ABSTRACT

Part I

Electronic absorption and emission spectra of polyenes, *all-trans* vitamin A alcohol, *all-trans* vitamin A acetate, β-apo-8'-carotenal, astacene and methyl bixin have been investigated in the solid state. On adsorption of certain vapours on the crystallite surfaces of these polyenes, a new band appears on the low energy side of the well known intense $^1A_g \longrightarrow {}^1B_u$ transition. No significant change in position of this new band is observed with adsorption of different vapours. A good mirror image relationship between the new absorption band and the well known emission band for these molecules indicates that this new absorption band may be due to a transition from the ground state to a low-lying π-electronic state wherefrom the emission initiates. The effect of different solvents on the intense $^1A_g \longrightarrow {}^1B_u$ transition and on the observed emission band of each polyene under investigation is appreciably different. This suggests that different excited states are involved in the absorption and in the emission processes. It has been concluded that in these long-chain polyenes there exists a low-lying forbidden ^1A_g state below the strongly allowed ^1B_u state.

On adsorption of some electron acceptor molecules on the solid films of the polyenes, in addition to the original bands, a new absorption band appears in each case on the longer wavelength side of the spectrum. This new band is energetically much lower than

the emission band of the molecules. The position of this new band is dependent on the electron affinity (E_A) of the acceptor molecules and the intensity depends on the amount of acceptor molecules adsorbed. A linear relationship between the $\bar{\nu}_{max}$ of the new band and E_A has been observed. The ionization potentials of the polyenes have been estimated from this linear relationship. The estimated values agree satisfactorily with the values obtained by other methods. It has been concluded that the polyenes behave as electron donors and in the solid state form charge-transfer complexes with suitable electron acceptors.

Part II

The change in semiconductive properties of some polyenes after adsorption of various vapours on the crystallite surface has been studied at constant sample temperatures. A rapid enhancement in the semiconduction current has been observed. The rise in conductivity has been found to be exponential with increasing vapour pressure of the adsorbed vapour. This adsorption process has been observed to be efficiently reversible. The adsorption and desorption kinetics have been found to follow the modified Roginsky-Zeldovich relation $dm/dt = A \exp(-\beta m/kT)$ where, m is the amount of vapour adsorbed at time 't', A and β are constants at a particular pressure. The activation energies of adsorption and desorption have been estimated from kinetic data analysis. A two-stage adsorption process satisfactorily explains the experimental results.

The change in semiconduction activation energy on adsorption of various vapours has been investigated. The adsorbed vapours change the activation energy by increasing or decreasing it. Such change depends on the chemical nature, amount of the vapour adsorbed and also on the polyene end group. These semiconductors follow the three-constant equation

$$\sigma(T) = \sigma_0' \exp(E/2kT_0) \exp(-E/2kT)$$

where the conventional pre-exponential factor σ_0 has been replaced by $\sigma_0' \exp(E/2kT_0)$ (the so called compensation effect). Here T_0 and σ_0' are constants for a particular substance and T_0 is called the characteristic temperature. T_0 has been found to play a significant role on the dark conduction process. Various methods used for evaluating T_0 and σ_0' have yielded consistent results. Excellent correlation obtained between the relevant parameters in these semiconductors indicates that σ_0 and E are physically related. Various models for conduction mechanism leading to compensation effect have been discussed.