DIPOLE MOMENT AND POLARIZABILITY

Introduction: The knowledge of the structure of molecules-their size, shape, array of atoms and spatial distribution, etc. is acquired these days from an application of refined physical methods. We have seen how interatomic distances and arrangement of atoms in a crystal are obtained from electron and X-ray diffraction studies. In this chapter, we shall only make an outline of the application of several other physical methods to find out the molecular structure. It is true that very often several methods are to be used jointly to have an idea of the structure.

Polar molecules

Molecules are composed of positively charged nuclei and negatively charged electrons distributed in space. The structural arrangement of these particles is different for different molecules. It will be easily conceived that the centre of gravity of the positive nuclei may or may not coincide with that of the negative electrons. When the centre of gravity of the positive charges in a molecule is exactly at the same point as that of the electrons, it is a non-polar molecule. Instances of non-polar molecules are found in H_2, Cl_2, N_2, CO_2, CH_4, C_6H_6, etc. On the other hand, in, many molecules like those HCl, CH_3Cl $CHCl_3$, $C_6H_5NO_2$, H_2O, NH_3, etc. the centres of gravity of the positive and the negative charges do not coincide; such molecules are said to be polar molecules.

Since the molecule as a whole is neutral, if we have a total charge +*e* at the centre of positive charges, the charge at the centre of negative charges would be -*e*. If *l* be the distance between the two centres of gravity in a polar molecule, it is said to have a permanent electric moment called the dipole moment (μ) given by,

$$\mu = e \times l \qquad \text{.............................(1)}$$

In a non-polar molecule the distance *l*=0 so that the dipole moment is nil. The charge of an electron is 4.7×10^{-10} e.s.u and the distance between the centres is of the order 10^{-8} cm. Hence the dipole moment is of the order of 10^{-18} esu of moment. It is often called a Debye unit; 1 Debye unit = 10^{-18} esu-cm.

Clausius -Mossotti Relation

Every molecule is made up of positively charged nuclei and negatively charged electron cloud as shown in Fig. 1(a) . The centre of positive charge coincides with the centre of negative charge. Hence when such a molecule is introduced between the two plates of an electric field, the positively charged nuclei and hence the centre of positive charge is attracted towards the negative plate, whereas the negatively charged electron cloud is attracted towards the positive plate of the electric field. As a result, the molecule gets distorted, as shown in Fig. 1(b) . This is called *polarization* of the molecule and the distorted molecule with positive and negative ends is called an *electric dipole*. The molecule remains polarized so long as the electric field is applied but goes back to the original state as soon as the electric field is switched off. That is why this type of polarization is called induced polarization and the electric dipole formed is called *induced dipole*.

Since even after polarization, the molecule is neutral as a whole, this means that the positive charge on one end must be equal to the negative charge on the other. Suppose this charge is q. If d is the distance of separation between the

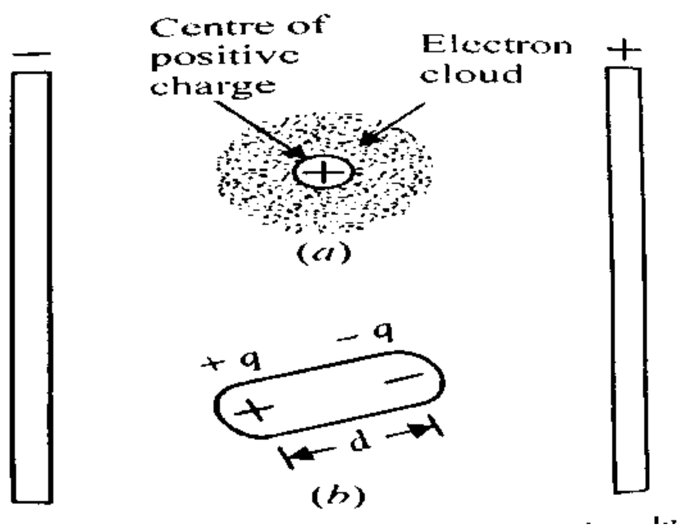

Fig. 1 Polarization of molecule an electric field (a) original state (b) polarized state.

charges, then dipole moment of the induced dipole μ will be given by

$\mu_i = q \times d$ .... (2)

Evidently, the value of μ_i, depend upon the nature of the molecule and the strength of the electric field, say X. Thus

$$\mu_i = \alpha \times X \qquad \text{.. (3)}$$

where α is a constant called polarizability of the given molecule.

α is found to be related to the dielectric constant, D of the medium present between the plates i.e the molecules being studied. According to the equation given by **Clausius and Mossotti**

$$(D - 1)/(D + 2))\ M/\rho = 4/3\ \pi N\alpha \qquad \text{.......................................(4)}$$

where M is molecular mass of the molecules
ρ the density of the molecules
N is Avogadro's number.

As all quantities on the right hand side of eqn. (4) are constant (α being constant for a substance) independent of temperature, therefore, the quantity on the left hand side of eqn. (4) must also be constant, independent of temperature and depending only upon the nature of the molecules. This quantity is called induced molar polarization and is represented by P_i.

Thus $P_i = (D - 1)/(D + 2)\ M/\rho$ .... (5)

Induced molar polarization is defined as the amount of polarization produced in 1 mole of the substance when placed between the plates of an electric field of unit strength

Using eqn. (5), the values of molar polarization have been determined for a number substances. It is found that whereas molar polarization of a number of substances such as O_2, CO_2, N_2 and CH_4 are constant and independent of temperature, the polarization values for some other substances such as HCl, $CHCl_3$, $C_6H_5NO_2$ and CH_3Cl do not come out to be constant, but decrease with increase of temperature.

In case of molecules such as HCI, $CHCl_3$, etc., their centres of positive and negative charges do not coincide with each other. Thus they possess some dipole moment even in the absence of electric field. The dipole moment thus possessed by the molecules is called *permanent dipole moment* in the absence of electric field these permanent dipoles are oriented in a random manner as shown in Fig. 2 . However in the presence of an electric field, two disturbing effects take place.

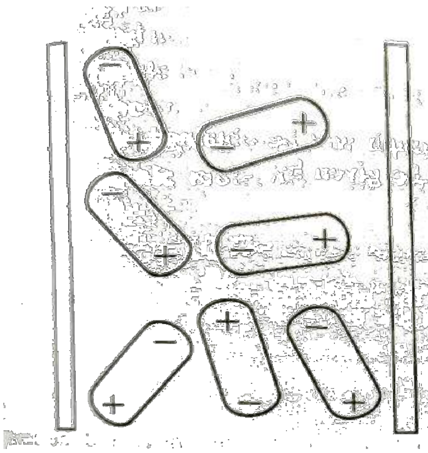

Fig 2: Permanent dipoles oriented in a random manner in the absence of an electric field

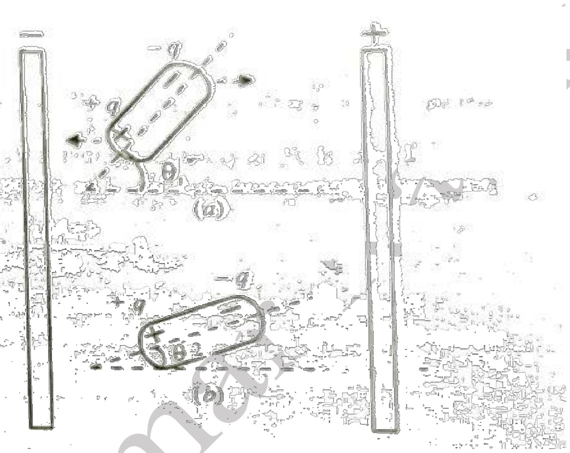

Fig 3: (a) Original state of a permanent dipole (b) Final state after polarization and orientation

These are

(1) The electric field will tend to rotate and orient these dipoles in the direction of the field.

(2) The electric field will tend to polarize the molecules.

If the molecules were stationary, the dipoles would have been oriented perfectly parallel to the electric field i.e, at right angles to the plates of the electric field. However, due to thermal agitation, they take up position in between that of the original state and the perfectly parallel state, as shown at (b) in Fig. 3 for any one permanent dipole.

Thus in case of molecules possessing permanent dipoles, the right-hand side of eq 5 will give the total polarization (P_t) which will be the sum of the induced molar polarization (P_i) and the orientation molar polarization (P_o)

$$\mathbf{P_t = (D - 1)/(D + 2)\, M/\rho = P_i + P_o} \quad \text{...} (6)$$

i.e. And, the induced polarization is given by (eq 4)

$$\mathbf{P_o=(4/3)\pi N\alpha} \quad \text{...} (7)$$

The orientation molar polarization is given by the equation put forward by Debye, viz,

$$P_i=(4/3)\pi N\ (\mu^2/3kT) \qquad \text{...} (8)$$

where μ is the *permanent dipole moment* of the molecule, *k* is Boltzmann's constant (=R/N) and T is the temperature. Substituting the values of P_i and P_o from equations (7) and (8) in eqn. (6), we get

$$P_t = (D - 1)/(D + 2)\ M/\rho\ =(4/3)\pi N\alpha\ +\ (4/3)\pi N\ (\mu^2/3kT) \qquad \text{.....................................} (9)$$

This equation can be written in the form

$$P_t = A + B/T \qquad \text{......................................} (10)$$

where $A = (4/3)\pi N\alpha$ and $B = 4\pi N\ \mu^2/9k$ are constant for the given substance.

Thus, if P_t is plotted against 1/T, a straight line graph will be obtained, if the molecules possessed permanent dipoles. The slope of the plot will be given by

$$B = 4\pi N\ \mu^2/9k \qquad \text{.....................................} (11)$$

From this eqn. the permanent dipole moment of the molecule can be calculated, as all other quantities are constants whose values are known.

This is true is amply proved from experiments, as indicated in Fig. 4 in which P_t, vs 1/T is plotted for several substances.

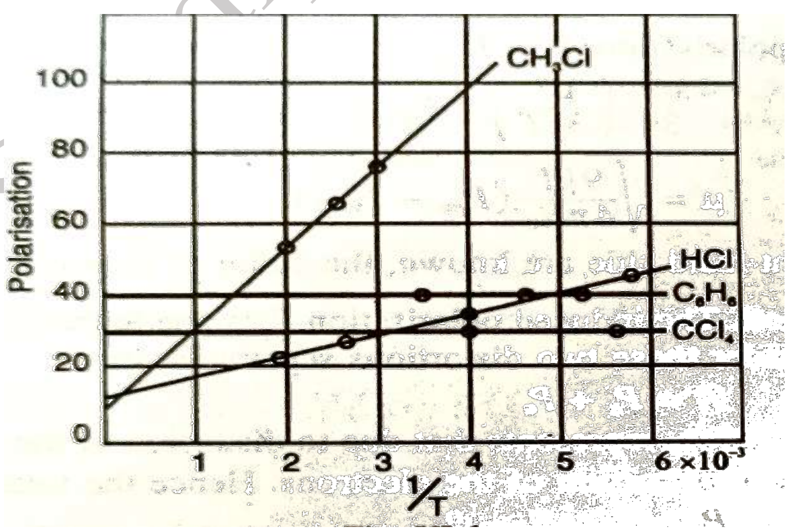

Figure 4

The plots in cases of and C_6H_6 and CCl_4 are found to be parallel to 1/T axis indicating their temperature independence and non-polar character. The graphs of CH_3Cl and HCI show that P_t varies linearly with 1/T. The slopes of these lines give the value of b of equation 10 and hence the dipole moment (μ) is known.