

## On the evaluation of dipole moment using Guggenheim's method

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Guggenheim's method for the determination of dipole moment of a polar solute in a nonpolar solvent is widely used because it avoids the measurement of density of different dilute solutions. In the present note it has been shown that formula for Guggenheim's method can also be derived from Debye equation on the assumption that the dielectric constant of the solvent is equal to the square of its refractive index.

### 1. INTRODUCTION

The determination of dipole moment of a polar solute in a nonpolar solvent through dielectric measurements gives a value in close agreement with the gaseous value. It is simply because of the fact that in such a situation, the system is in a quasi-isolated state and the polar molecules are well separated from each other such that the dipole-dipole interaction forces are absent. Various methods (Debye 1929, Halverstadt & Kumler 1942, Higasi 1943, Guggenheim 1949, Smith 1950, Guggenheim 1951) have been proposed for determining the dipole moment of a polar solute in a nonpolar solvent. The method suggested by Guggenheim (1951) is widely used (Murty 1957, Purcell & Singer 1965) because it avoids the measurement of density of different dilute solutions. However, it has recently been shown by Bock & Iwacha (1968) that for solute molecules, having a low dipole moment value, Guggenheim's method does not give reasonable results. Further, using partial quantity to dielectric polarization, Palit (1952) has established, that Guggenheim's method is a special case of the more general Palit's method. This discrepancy may be due to the fact that the Guggenheim's method is derivable from Debye equation which is valid only for very dilute polar non-polar mixtures. The purpose of the present note is to show that the formula used in the Guggenheim's method can be derived from the Debye equation under the assumption that the dielectric constant of the solvent is equal to the square of its refractive index.

2. METHOD OF CALCULATION

The dielectric behaviour of a polar solute in a nonpolar solvent can very well be represented with the help of Debye's relation (Debye 1929) as

$$\frac{\epsilon_{012}-1}{\epsilon_{012}+2} = \frac{n^2_{D12}-1}{n^2_{D12}+2} + \frac{4\pi n\mu^2}{9kT}, \quad \dots (1)$$

where  $\epsilon_0$  is the static dielectric constant,  $n_D$  is the refractive index measured at a frequency off from the dielectric dispersion region,  $n$  is the number of solute molecules per c.c., and  $\mu$  is its dipolemoment. Suffix 12 represents the solution. The above expression can be rearranged as

$$\begin{aligned} X &= \frac{4\pi N\mu^2 d_{12}}{27 M_2 kT} w_2, \quad \dots (2) \\ &= \frac{\epsilon_{012}-n^2_{D12}}{(\epsilon_{012}+2)(n^2_{D12}+2)}. \end{aligned}$$

In eq. (2),  $d$  is the density,  $w_2$  is the weight fraction of the solute molecule and  $M_2$  is its molecular weight. Eq. (2) could be used for determining the value of  $\mu$  if density of different dilute solutions are measured. Such measurements of density are avoided if we use very dilute solutions as shown in the following paragraphs.

It can be seen that for infinitely dilute solution i.e., when  $w_2 \rightarrow 0$  eq. (2) reduces to

$$\left( \frac{\partial X}{\partial w_2} \right)_{w_2 \rightarrow 0} = \frac{4\pi N\mu^2 d_1}{27 M_2 kT}, \quad \dots (3)$$

where suffix 1 stands to represent the solvent. Eq. (3) is an equation of a straight line provided the measurements are done at a fixed temperature. It suggests, therefore, that when  $X$  is plotted against  $w_2$  for different dilute solutions, it will result into a straight line, the slope of which at  $w_2 \rightarrow 0$  gives the value of  $\mu$ . However, it has been pointed out by LeFevre (1950) that smoothing should be performed directly on the measured quantities such as  $\epsilon_{012}$  and  $n_{D12}$  rather than on any derived parameter. The value of  $X$  in terms of  $\epsilon_{012}$  and  $n_{D12}$  will be

$$\left( \frac{\partial X}{\partial w_2} \right)_{w_2 \rightarrow 0} = \left[ \frac{1}{(\epsilon_{01}+2)^2} \left( \frac{\partial \epsilon_{012}}{\partial w_2} \right)_{w_2 \rightarrow 0} - \frac{2n_{D1}}{(n^2_{D1}+2)^2} \left( \frac{\partial n_{D12}}{\partial w_2} \right)_{w_2 \rightarrow 0} \right]. \quad \dots (4)$$

If we assume at this stage that for solvent the static dielectric constant is equal to square of its refractive index i.e.,  $\epsilon_{01} = n^2_{D1}$ , eq. (4) combined with eq. (3) can be written as

$$\left( \frac{\mu}{\text{Debye}} \right)^2 = \frac{10^{36}}{N} \cdot \frac{9kT}{4\pi} \cdot \frac{M_2}{d_1} \cdot \frac{3}{(\epsilon_{01}+2)^2} \cdot \left( \frac{\Delta}{w_2} \right)_{w_2 \rightarrow 0} \quad \dots (5)$$

where

$$\left(\frac{\Delta}{w_2}\right)_{w_2 \rightarrow 0} = \left[ \left(\frac{\partial \epsilon_{012}}{\partial w_2}\right)_{w_2 \rightarrow 0} - 2n_{D1} \left(\frac{\partial n_{D12}}{\partial w_2}\right)_{w_2 \rightarrow 0} \right]$$

Thus the value of  $\mu$  can be evaluated with the help of eq. (5). It can be remarked here that the use of modified form of Debye equation avoids the measurement of density of different dilute solutions and needs only the density of solvent at experimental temperature. Eq. (5) is evidently representing the Guggenheim's equation manifesting the fact that Guggenheim's method can be derived from Debye equation following the assumption  $\epsilon_{01} = n^2_{D1}$ .

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