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**A MATHEMATICAL EXTRAPOLATION METHOD  
FOR COMPLEX DIELECTRIC  
POLARISATION DATA**

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**Abstract**

A mathematical extrapolation method has been outlined and applied to complex dielectric polarisation data on dilute solutions of a polar molecule in a non-polar solvent. It is shown that accurate values of both the dipole moment and relaxation time of molecules may be obtained from measurements employing even one frequency alone very near the absorption region.

**1. Introduction**

The dilute solution method of determining the dielectric polarisation of a polar solute in a non-polar solvent is one that is often used in the determination of dipole moments of molecules from dielectric constant and density data of solutions of known concentrations. The dielectric constants of the solutions are measured usually in the frequency region where there is not much or little of absorption and dispersion or in other words, in a region where the solute dipoles are able to follow the applied field. The total polarisation of the solute is then found out by extrapolation to infinite dilution of the solution either by graphical or mathematical methods. As the frequency of the applied field is increased we

encounter the well-known phenomenon of anomalous dispersion and absorption due to the fact that the dipoles are not able to follow the field in the same way as at lower frequencies. Debye (1929) has shown that the dielectric constant  $\epsilon$  at these frequencies may be split up into two parts, the real ( $\epsilon'$ ) and the imaginary ( $\epsilon''$ ), the latter being a measure of the absorption. The total polarisation could also be split up into  $P_r$  and  $P_i$  corresponding respectively to the real and imaginary parts and the extrapolation of the total polarisation to infinite dilution has to be done separately for  $P_r$  and  $P_i$ . Potapenko and Wheeler (1948) employed the graphical method of extrapolating  $P_r$  and  $P_i$  and obtained satisfactory values for the dipole moment,  $\mu$  and relaxation time,  $\tau$  of some organic acid molecules in dioxan from dielectric measurements at high frequencies. The limitations of the graphical method in general need not be emphasized here since the great drawback in this method arises from the fact that it is largely subjective and not as accurate as mathematical methods. Mathematical extrapolation formulae have been developed by Hedestrand (1929), Halverstadt and Kumler (1942) and several others for use in the non-absorbing regions, but there is no mathematical method for extrapolating the dielectric polarisation data obtained in the region of absorption. Such a formula would provide us with an accurate method of determining the dipole moment and relaxation time of molecules from measurements even at a single frequency where  $\epsilon'$  and  $\epsilon''$  could be accurately measured. In this paper a mathematical formula for extrapolation of high frequency dielectric polarisation data has been developed on lines similar to those of Hedestrand.

## 2. Extrapolation at Low Frequencies

The total polarisation  $P_{12}$  of a solution of a polar solute in a non-polar solvent is usually written as

$$P_{12} = P_1 f_1 + P_2 f_2 = \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \cdot \frac{M_1 f_1 + M_2 f_2}{d_{12}} \quad \dots (1)$$

(In this paper  $\epsilon$  and  $d$  always refer to the dielectric constant

and density and the subscripts 1, 2 and 12 refer to the solvent, solute and solution respectively.

$f$  = mole fraction).

Since the solvent is non-polar  $P_1$  is a constant and at very high dilutions where there would be no dipole interaction  $P_2$  should be also constant. The  $P_{12}$  vs  $f_2$  plot would give, on linear extrapolation to  $f_2 = 0$ , the values of  $P_1$  and  $P_2$  from the intercept and slope respectively. This is the principle of the graphical method of extrapolation. Owing to the non-linearity of the  $P_{12}$  vs  $f_2$  plot in many cases this method often leads to great error. A better method is to extrapolate  $P_{12}$  mathematically to  $f_2 = 0$  using the functional relationship between  $\epsilon_{12}$ ,  $d_{12}$  and  $f_2$  as has been shown by Hedestrand. Since the formulae derived in this paper for use in the anomalous region are based essentially on that of Hedestrand's a short derivation of this is given below.

From equation (1) it follows that

$$P_2 = \frac{P_{12} - f_1 P_1}{f_2} \quad \dots (2)$$

Inserting equation (2) in equation (1) we get

$$P_2 = \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \cdot \frac{M_2}{d_{12}} + \frac{M_1 f_1}{f_2} \left\{ \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \cdot \frac{1}{d_{12}} - \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \frac{1}{d_1} \right\} \dots (3)$$

The existing mass of experimental data point out to a simple relationship between  $\epsilon_{12}$ ,  $d_{12}$  and  $f_2$  of the form given below.

$$\epsilon_{12} = \epsilon_1 (1 + \alpha f_2) \quad \dots (4a)$$

$$d_{12} = d_1 (1 + \beta f_2) \quad \dots (4b)$$

where  $\alpha$  and  $\beta$  are constants.

Substituting equations (4a) and (4b) in (3) we get on rearranging

$$P_2 = \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \cdot \frac{M_2}{d_{12}} + \frac{M_1 f_1}{d_{12}} \left\{ \frac{3 \alpha \epsilon_1 - \beta (\epsilon_1 - 1) [\epsilon_1 (1 + \alpha f_2) + 2]}{[\epsilon_1 (1 + \alpha f_2) + 2] [\epsilon_1 + 2]} \right\} \dots (5)$$

Now,  $\lim_{f_2 \rightarrow 0} P_2 = P_2^\infty$  and  $\lim_{f_2 \rightarrow 0} \epsilon_{12} = \epsilon_1$ . Further  $\lim_{f_2 \rightarrow 0} d_{12} = d_1$

and  $\lim_{f_2 \rightarrow 0} f_1 = 1$ . Thus we get,

$$P_2^\infty = \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \frac{M_2}{d_1} + \frac{M_1 [3 \alpha \epsilon_1 - \beta (\epsilon_1 - 1) (\epsilon_1 + 2)]}{d_1 (\epsilon_1 + 2)^2} \dots (6)$$

$$\text{or } P_{\infty} = \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \frac{M_2 - \beta M_1}{d_1} + \frac{3 M_1 \alpha \epsilon_1}{d_1 (\epsilon_1 + 2)^2} \quad \dots (7)$$

Equation (7) is the well-known Hedestrand's formula.

### 3. Extrapolation in the Anomalous Region

As already stated in the region of absorption the dielectric constant  $\epsilon$  and the polarisation  $P$  are complex in the sense that  $\epsilon = \epsilon' - i\epsilon''$  and  $P = P_r - iP_i$ . Consequently the extrapolation has to be carried out separately for  $P_r$  and  $P_i$ .  $P_r$  and  $P_i$  may be shown (Potapenko and Wheeler 1948) to be

$$P_{r_{12}} = \frac{\epsilon_{12}'^2 + \epsilon_{12}'' + \epsilon_{12}''^2 - 2}{\epsilon_{12}'^2 + 4\epsilon_{12}' + \epsilon_{12}''^2 + 4} \cdot \frac{M_1 f_1 + M_2 f_2}{d_{12}} \quad \dots (8)$$

$$P_{i_{12}} = \frac{3\epsilon_{12}''}{\epsilon_{12}'^2 + 4\epsilon_{12}' + \epsilon_{12}''^2 + 4} \cdot \frac{M_1 f_1 + M_2 f_2}{d_{12}} \quad \dots (9)$$

obtained by substituting the complex expressions for  $\epsilon$  and  $P$  in equation (1). From the plots of  $P_{r_{12}}$  vs  $f_2$  and  $P_{i_{12}}$  vs  $f_2$  we may find the values of  $P_{r_2\infty}$  and  $P_{i_2\infty}$  corresponding to  $f_2 = 0$ . As mentioned earlier this method has serious drawbacks and we shall therefore derive mathematical formulae for the evaluation of  $P_{r_2\infty}$  and  $P_{i_2\infty}$ . For this purpose we need an expression relating  $\epsilon_{12}'$ ,  $\epsilon_{12}''$  and  $d_{12}$  with  $f_2$ . It is obvious that equation (4b) for density is valid in the present problem and may therefore be used as such. Only recently has the dependence of  $\epsilon_{12}'$  and  $\epsilon_{12}''$  on  $f_2$  been studied carefully and from a detailed and accurate investigation of the microwave absorption of dilute solutions of several organic compounds in non-polar solvents Heston, Franklin, Hennelly and Smyth (1950) have shown that a relationship of the form expressed in equation (10) below exists.

$$\epsilon_{12}' = \epsilon_1' + x f_2 \quad \dots (10a)$$

$$\epsilon_{12}'' = y f_2 \quad \dots (10b)$$

where  $x$  and  $y$  are constants. With these expressions on hand we can now proceed to find out mathematical extrapolation formulae for  $P_{r_2\infty}$  and  $P_{i_2\infty}$ .

It can be shown that

$$P_{r_1} = \frac{\epsilon_1' - 1}{\epsilon_1' + 2} \cdot \frac{M_1}{d_1} \quad \dots (11)$$

even in the region of absorption since  $\epsilon_1''=0$ , the solvent being non-polar. Assuming that the law of additivity holds for  $P_r$  as for  $P$  in equation (2) we may write

$$P_{r_2} = \frac{P_{r_{12}} - f_1 P_{r_1}}{f_2} \quad \dots (12)$$

Substituting equations (8) and (11) in (12) we get

$$P_{r_2} = \frac{\epsilon_{12}'^2 + \epsilon_{12}' + \epsilon_{12}''^2 - 2}{\epsilon_{12}'^2 + 4\epsilon_{12}' + \epsilon_{12}''^2 + 4} \cdot \frac{M_1 f_1 + M_2 f_2}{d_{12}} \cdot \frac{1}{f_2} - \frac{M_1 f_1}{d_1} \cdot \frac{\epsilon_1' - 1}{\epsilon_1' + 2} \cdot \frac{1}{f_2} \quad \dots (13)$$

Equation (13) may be re-written as

$$P_{r_2} = \frac{\epsilon_{12}'^2 + \epsilon_{12}' + \epsilon_{12}''^2 - 2}{\epsilon_{12}'^2 + 4\epsilon_{12}' + \epsilon_{12}''^2 + 4} \cdot \frac{M_2}{d_{12}} + \frac{M_1 f_1}{f_2} \left\{ \frac{\epsilon_{12}'^2 + \epsilon_{12}' + \epsilon_{12}''^2 - 2}{\epsilon_{12}'^2 + 4\epsilon_{12}' + \epsilon_{12}''^2 + 4} \cdot \frac{1}{d_{12}} - \frac{\epsilon_1' - 1}{\epsilon_1' + 2} \cdot \frac{1}{d_1} \right\} \quad \dots (14)$$

Substitution of equation (10a), (10b) and (4b) in (14) gives on rearrangement

$$P_{r_2} = \frac{(\epsilon_1' + x f_2)^2 + (\epsilon_1' + x f_2) + (y f_2)^2 - 2}{(\epsilon_1' + x f_2)^2 + 4(\epsilon_1' + x f_2) + (y f_2)^2 + 4} \cdot \frac{M_2}{d_{12}} + \frac{M_1 f_1}{d_{12}} \left[ \frac{A}{\Delta} \right] \quad \dots (15)$$

where  $A$  and  $\Delta$  may be shown on expansion to be

$$A = 3x(\epsilon_1' + x f_2 + 2) - \beta \epsilon_1' [\epsilon_1''^2 - 4\epsilon_1' + 2x f_2 \epsilon_1' - 4x f_2 + (x f_2)^2 + (y f_2)^2] + \beta [\epsilon_1' + 4x f_2 + (x f_2)^2 + (y f_2)^2 + 4] + 3y^2 f_2 \quad \dots (16)$$

$$\Delta = \epsilon_1''^2 + 6\epsilon_1'' + 12\epsilon_1' + \epsilon_1' [6x f_2 + (x f_2)^2 + (y f_2)^2] + 12x f_2 + 2[(x f_2)^2 + (y f_2)^2] + 8 \quad \dots (17)$$

Now,  $\lim_{f_2 \rightarrow 0} P_{r_2} = P_{r_2 \infty}$  and  $\lim_{f_2 \rightarrow 0} \epsilon_{12}' = \epsilon_1'$ .

We have also  $\lim_{f_2 \rightarrow 0} d_{12} = d_1$  and  $\lim_{f_2 \rightarrow 0} f_1 = 1$ . Thus

at  $\lim_{f_2 \rightarrow 0}$  equation (15) becomes

$$P_{r_2 \infty} = \frac{\epsilon_1'^2 + \epsilon_1' - 2}{(\epsilon_1' + 2)^2} \cdot \frac{M_2}{d_1} + \frac{M_1}{d_1} \left\{ \frac{3x(\epsilon_1' + 2) - \beta(\epsilon_1''^3 - 4\epsilon_1''^2 + \epsilon_1' + 4)}{\epsilon_1'(\epsilon_1''^2 + 6\epsilon_1'' + 12) + 8} \right\} \quad \dots (18)$$

The experimentally determined values of  $x$  and  $\beta$  may be inserted in equation (18) and the value of  $P_{r_2 \infty}$  obtained as in the case of equation (6).

Having thus obtained an expression for  $P_{r_2\infty}$  we may now derive a similar expression for  $P_{i_2\infty}$ . Since we are primarily interested in a non-polar solvent whose  $\epsilon_1'' = 0$  we may write

$$P_{i_2} = \frac{P_{i_2}}{f_2} \quad \dots (19)$$

Inserting equation (9) in (19) and making use of equations (10a), (10b) and (4b) we get

$$P_{i_2} = \frac{M_1 f_1}{d_1 (1 + \beta f_2)} \cdot \frac{1}{f_2} \left\{ \frac{3 y f_2}{(\epsilon_1' + x f_2)^2 + 4 (\epsilon_1' + x f_2) + (y f_2)^2 + 4} \right\} \\ + \frac{M_2 f_2}{d_1 (1 + \beta f_2)} \cdot \frac{1}{f_2} \left\{ \frac{3 y f_2}{(\epsilon_1' + x f_2)^2 + 4 (\epsilon_1' + x f_2) + (y f_2)^2 + 4} \right\} \dots (20)$$

Now,  $\lim_{f_2 \rightarrow 0} f_1 = 1$  and making use of this relation in equation (20)

we find that while at  $\lim_{f_2 \rightarrow 0}$  the second term in the right hand side of equation (20) vanishes, we get finally on rearranging

$$P_{i_2\infty} = \frac{3 y M_1}{d_1 (\epsilon_1' + 2)^2} \quad \dots (21)$$

The values of  $P_{r_2\infty}$  and  $P_{i_2\infty}$  obtained from equations (18) and (21) may be now used for the calculation of the dipole moment and relaxation time of molecules from measurements on dilute solutions using even a single frequency near the region of absorption just as in the case of the more familiar dielectric measurements at low frequencies.

It has been shown by Debye (1929) that

$$P_{T\infty} = P_D + P_0 \left( \frac{1}{1 + i \omega \tau} \right) \quad \dots (22)$$

where  $P_{T\infty}$  = the total polarisation of the solute at infinite dilution,  $P_D$  = the distortion polarisation and  $P_0$  = the orientation polarisation.  $\omega = 2 \pi$  times the frequency used and  $\tau$  = the relaxation time of the dipole. At lower frequencies equation (22) becomes

$$P_{T\infty} = P_D + P_0 \quad \dots (23)$$

Following Potapenko and Wheeler (1948) we find that since

$$P_{r_2\infty} = P_{T\infty} - P_0 \left( \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \right) \quad \dots (24)$$

$$\text{and } P_{i_2\infty} = P_0 \left( \frac{\omega \tau}{1 + \omega^2 \tau^2} \right) \quad \dots (25)$$

Substituting equation (23) in (24) and solving the resulting equation simultaneously with (25) we get

$$P_0 = \frac{P_{i_2 \infty} + (P_{r_2 \infty} - P_D)^2}{P_{r_2 \infty} - P_D} \quad \dots (26)$$

$$\text{and } \tau = \frac{1}{\omega} \cdot \frac{P_{i_2 \infty}}{P_{r_2 \infty} - P_D} \quad \dots (27)$$

The dipole moment,  $\mu$ , may be obtained from the equation  $\mu = 0.0127 \sqrt{P_0 \cdot T}$  ( $T$  = the absolute temperature), the value of  $P_0$  being taken from equation (26). The magnitude of  $P_D$  may be determined as usual from refractive index measurements.

#### 4. Analysis of Experimental Data

Most of the experimental data available in the literature are insufficient for the calculation of  $\mu$  and  $\tau$  by the present method chiefly due to the lack of  $\epsilon''$  and  $\beta$  values. However, Franklin, Heston, Hennelly and Smyth (1950) have recorded a large number of  $x$ ,  $y$  and  $\beta$  values at various temperatures for some organic compounds in non-polar solvents in the microwave region. Using the values of these authors the dipole moments of some substances were calculated using equations (18), (21) and (26) and found to agree remarkably well with existing data at low frequencies. Tables I, II and III showing the calculated values of dipole moment,  $\mu$  and relaxation time,  $\tau$  of ethyl bromide in various solvents are typical of those obtained by the use of the present mathematical extrapolation method.

**Table I**  
**C<sub>2</sub>H<sub>5</sub>Br — C<sub>7</sub>H<sub>16</sub>**

Solvent	Temp.	$\lambda_0$ in cms.	$x$	$y$	$\beta$	$P_{r_2 \infty}$ calcd. in c.c.	$P_{i_2 \infty}$ calcd. in c.c.	$P_0$ calcd. in c.c.	$\mu$ calcd. $\times 10^{-18}$ e.s.u.	$\tau$ calcd. $\times 10^{-12}$ sec.
$\epsilon_1' = 1.923$	20° C	1.277	2.80	0.66	0.541	119.80	18.85	94.24	2.11	1.42
$d_1 = 0.6838$	"	3.22	2.76	0.36	0.541	118.65	10.28	90.34	2.07	
$\epsilon_1' = 1.895$	40° C	1.277	2.40	0.56	0.555	111.27	16.65	85.16	2.07	2.04
$d_1 = 0.6665$	"	3.22	2.49	0.27	0.555	113.95	8.03	85.21	2.07	

$\mu$  calculated from 577 m. data = 1.88D (20°C) and 1.95D (40°C) using Hedestrand's method.

$\tau$  (Franklin et. al.) =  $1.6 \times 10^{-12}$  secs.

**Table II**  
 $C_2H_5Br - C_6H_{12}$

Solvent	Temp.	$\lambda_0$ in cms.	$x$	$y$	$\beta$	$P_{r_2 \infty}$ calcd. in c.c.	$P_{i_2 \infty}$ calcd. in c.c.	$P_0$ calcd. in c.c.	$\mu$ calcd. $\times 10^{-18}$ e.s.u.	$\tau$ calcd. $\times 10^{-12}$ sec.
$\epsilon_1' = 2.026$	20° C	1.277	2.85	0.95	0.590	94.60	18.95	70.63	1.83	1.69
$d_1 = 0.7795$	„	3.22	3.73	0.60	0.590	111.69	11.69	83.94	1.99	
$\epsilon_1' = 1.992$	40° C	1.277	2.80	0.81	0.592	95.98	16.88	70.77	1.89	1.72
$d_1 = 0.7604$	„	3.22	3.39	0.45	0.592	115.22	9.38	86.75	2.09	

$\mu$  calculated from 577 m. data = 1.89D (20°C) and 1.95D (40°C) using Hedestrand's method.

$\tau$  (Franklin et. al) =  $2.1 \times 10^{-12}$  secs.

**Table III**  
 $C_2H_5Br - C_{16}H_{34}$

Solvent	Temp.	$\lambda_0$ in cms.	$x$	$y$	$\beta$	$P_{r_2 \infty}$ calcd. in c.c.	$P_{i_2 \infty}$ calcd. in c.c.	$P_0$ calcd. in c.c.	$\mu$ calcd. $\times 10^{-18}$ e.s.u.	$\tau$ calcd. $\times 10^{-12}$ sec.
$\epsilon_1' = 2.049$	20° C	1.277	1.20	0.33	0.220	102.80	14.99	76.37	1.90	1.39
$d_1 = 0.7740$	„	3.22	1.37	0.28	0.220	111.89	12.72	84.35	2.00	
$\epsilon_1' = 2.027$	40° C	1.277	0.95	0.25	0.224	91.09	13.78	64.67	1.81	1.52
$d_1 = 0.7597$	„	3.22	1.24	0.20	0.224	107.09	11.02	79.16	2.00	

$\mu$  calculated from 577 m. data = 1.79D (20°C) and 1.82D (40°C) using Hedestrand's method.

$\tau$  (Franklin et. al.) =  $2.1 \times 10^{-12}$  secs.

A value of 29.5 c.c. has been taken for  $P_D$  of ethyl bromide in the above calculations. (Smyth and Morgan 1928). An examination of the results obtained with the present method shows clearly that the calculated values of  $\mu$  are in good agreement with those obtained at lower frequencies. It is also clear that data obtained with one frequency alone are sufficient to enable us to calculate  $\mu$  and  $\tau$ . The values of  $\tau$  calculated from equation (27) have been found to be of the correct order but are found to vary in some cases by about  $\pm 0.5 \times 10^{-12}$  secs. for the two wavelengths listed above. It is not unlikely that such variations of the calculated  $\tau$  values are either due to a distribution of the relaxation time or



due to small errors in the values of  $y$  since these in turn would affect the  $P_{i, \infty}$  values adversely. The  $\tau$  values in the above tables have been calculated for  $\lambda_0 = 1.277$  cm. alone since the  $y$  values are larger in this case than for  $\lambda_0 = 3.22$  cm.

In conclusion it may be stated that the mathematical extrapolation formula derived in this paper may be used with great advantage in the calculation of  $\mu$  and  $\tau$  values from dielectric data on dilute solutions of a polar solute in a non-polar solvent in the region of absorption. The present method may be further modified along lines similar to those used by Halverstadt and Kumler (1942) and applied to a wider range of experimental data.

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