# DETERMINATION OF DIPOLE MOMENT IN SOLUTION *

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**ABSTRACT.** The apparent electric moment of ortho-, meta- and para-nitrotoluene is measured in each of the solvents hexane, heptane, carbon tetrachloride, benzene, toluene, carbon disulphide and chloroform. The results are used to verify the empirical relations of Müller, Sugden and Jenkins, and the theories of Frank and Higasi, which connect the measured value of the electric moment with the value in the gaseous state. It is found that (1) the Sugden relation $P_2 = A + B \frac{\epsilon - 1}{\epsilon + 2}$ can be used for determining polarization at infinite dilution; (2) the empirical relation $_\infty P_2 = a / \sqrt{\epsilon}(\text{solvent})$ represents the results as well as the relations of Sugden and Jenkins; (3) the idea of extrapolation to $\epsilon = 1$ for the gaseous state needs reconsideration since the values obtained from the relations of Sugden, Jenkins, Frank and the authors are widely different; (4) if a critical dielectric constant, which requires extrapolation to $\epsilon = 1.7$ for the gaseous state, is introduced as a hypothesis, there appears a general agreement between the values so derived from the relations of Sugden, Jenkins, Frank and the authors.

The apparent electric moment of ortho-, meta- and para-nitrotoluene was measured in each of the solvents hexane, heptane, carbon tetrachloride, benzene, toluene, carbon disulphide and chloroform at room temperature (30°C). These solvents cover a range of dielectric constant 1.878 to 4.795. Of them hexane, heptane, carbon tetrachloride, benzene and carbon disulphide may be regarded as non-polar, and toluene as slightly polar. Chloroform, which is decidedly polar, was selected to test the applicability of the empirical relations to polar solvents.

Hexane and heptane (both Kahlbaum) were kept over calcium chloride and distilled over phosphorus pentoxide.

Carbon tetrachloride (Merck) was distilled over phosphorus pentoxide.

Benzene (Kahlbaum—for analysis) was dried over sodium wire and fractionated.

Toluene (Kahlbaum) was dried over sodium wire and fractionated.

Carbon disulphide (Kahlbaum—for analysis) was distilled over phosphorus pentoxide.

Chloroform (Merck—anaesthetic) was distilled over phosphorus pentoxide.

Ortho- and meta-nitrotoluene (both Merck) were distilled.

Para-nitrotoluene (Merck) was recrystallised from benzene.

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In each case the solvent was distilled a few hours before using it and the use of stored samples was avoided. The values of the density, the refractive index and the dielectric constant are given in table I.

TABLE I

| Substance | Density | Refractive Index | Dielectric Constant |
|---|---|---|---|
| Hexane | 0.66680 | 1.3772 | 1.878 |
| Heptane | 0.71045 | 1.3972 | 1.942 |
| Carbon tetrachloride | 1.5756 | 1.4531 | 2.212 |
| Benzene | 0.86588 | 1.4032 | 2.262 |
| Toluene | 0.86404 | 1.4892 | 2.358 |
| Carbon disulphide | 1.2542 | 1.6200 | 2.648 |
| Chloroform | 1.4699 | 1.4389 | 4.795 |
| o-nitrotoluene | 1.1548 | 1.5422 | ... |
| m-nitrotoluene | 1.1484 | 1.5424 | ... |

The apparatus and procedure were the same as employed in previous work [1].

The total molar polarization $P_2$ of a solute in a non-polar solvent is usually calculated from the Debye equation

$$P_2 = \frac{1}{f_2}\left[\frac{\epsilon-1}{\epsilon+2}\cdot\frac{M_1 f_1 + M_2 f_2}{d} - \frac{\epsilon_1-1}{\epsilon_1+2}\frac{M_1}{d_1}\cdot f_1\right]$$

When $P_2$ varies with $f_2$, the polarization at infinite dilution $_\infty P_2$ is determined from the $P_2$—$f_2$ curves extrapolated to $f_2 = 0$. To avoid this graphical extrapolation, Hedestrand [2] has introduced the method of mathematical extrapolation which assumes a linear variation of the density and the dielectric constant of the solution with the mole-fraction of the solute at low concentrations. Thus $\epsilon = \epsilon_1(1 + \alpha f_2)$ and $d = d_1(1 + \beta f_2)$ $_\infty P_2 = A$ $(M_2 - B\beta d_1) + C\alpha\epsilon_1$ where

$$A = \frac{\epsilon_1-1}{\epsilon_1+2}\frac{1}{d_1},\; B = \frac{M_1}{d_1} \quad\text{and}\quad C = \frac{3M_1}{d_1(\epsilon_1+2)^2}\;.$$

To avoid discrimination, polarization at infinite dilution was calculated using both the methods. The result is given in table II. The agreement between the two methods is good for ortho-nitrotoluene. For meta- and para-nitrotoluene the values exhibit differences. The disparity is more pronounced for para-nitrotoluene in the solvents hexane and heptane. Such differences might be attributed to the uncertainty involved in the extrapolation of the $P_2$—$f_2$ curves to $f_2 = 0$ wherever the curves are steep near $f_2 = 0$. Besides, $\alpha\epsilon_1$ and $\beta d_1$ do not always give constant values as might be expected from Hedestrand's assumption. In

such cases graphical extrapolation of $\alpha\epsilon_1$ and $\beta d_1$ to $f_2=0$ has to be used, and the values are subject to the inaccuracies of graphical methods. Hence, it was thought desirable to calculate $_\infty P_2$ by a method which does not involve curvilinear extrapolation to $f_2=0$. Since the variation of $\epsilon$ and $d$ with $f_2$ is not linear for some of the solutions, it was thought desirable to investigate the variation of $\epsilon$ and $d$ with the weight fraction or the volume fraction of the solute. For this purpose solution of ortho-nitrotoluene in benzene, which does not show the linear variation of $\epsilon$ and $d$ with $f_2$, was selected.

Le Fèvre [3] has used Hedestrand's method of mathematical extrapolation for calculating the specific polarization using weight fractions. Starting from the equation

$$p_2 = p_1 + \frac{1}{w_2}\left(\frac{\epsilon-1}{\epsilon+2}\frac{1}{d} - \frac{\epsilon_1-1}{\epsilon_1+2}\frac{1}{d_1}\right) \qquad \ldots \text{(1)}$$

proposed by Sugden [4], Le Fèvre assumes that the variation of $\epsilon$ and $d$ with $w_2$ (the weight fraction of the solute) is linear. Thus: $\epsilon = \epsilon_1(1+\alpha'w_2)$,

$$d = d_1\ (1+\beta'w_2) \text{ and } _\infty p_2 = p_1(1-\beta')+C\alpha'\epsilon_1,$$

where $\qquad p_1 = \dfrac{\epsilon_1-1}{\epsilon_1+2}\dfrac{1}{d_1} \qquad$ and $\qquad C = \dfrac{3}{d_1(\epsilon_1+2)^2}$.

When $\alpha'\epsilon_1$ and $\beta'd_1$ are calculated for $o$-nitrotoluene in benzene the values are not constant and graphical extrapolation is necessary. The specific polarization $_\infty p_2$ is 2.443 and the molar polarization $_\infty P_2 = M_2 p_2 = 335$ c.c.

Having failed so far in avoiding curvilinear extrapolation it was now thought necessary to develope other methods. It may be assumed that the variation of $\epsilon$ and $d$ with $V_2$ (the volume fraction of the solute) is linear. Such an assumption is supported by the mixture law for densities and Silberstein's formula for the dielectric constant of mixtures. Thus $\epsilon = \epsilon_1'(1+\alpha V_2)$ and $d = d_1(1+\beta V_2)$. Substituting for $\epsilon$ and $d$ in the Sugden relation (1), we have

$$p_2 = p_1 + \frac{1}{w_2 d}\cdot\frac{V_2[3\alpha\epsilon_1 - \beta(\epsilon_1-1)\{\epsilon_1(1+\alpha V_2)+2\}]}{\{\epsilon_1(1+\alpha V_2)+2\}(\epsilon_1+2)}.$$

Putting $V_2 = \dfrac{w_2 d_1}{d_2 + w_2 d_1 - w_2 d_2}$ and proceeding to the limit when $V_2 \rightarrow 0$,

$$_\infty p_2 = p_1 + \frac{1}{d_2}\cdot\frac{3\alpha\epsilon_1 - \beta(\epsilon_1-1)(\epsilon_1+2)}{(\epsilon_1+2)^2}$$

$$= p_1(1-\beta d_1 K) + KL\alpha\epsilon_1$$

where $\qquad p_1 = \dfrac{\epsilon_1-1}{\epsilon_1+2}\dfrac{1}{d_1}$; $\ K = \dfrac{1}{d_2}$ and $L = \dfrac{3}{(\epsilon_1+2)^2}$.

Again $a\epsilon_1$ and $\beta\epsilon_2$ calculated for $o$-nitrotoluene in benzene are not constant and graphical extrapolation is necessary. The specific polarization $_\alpha p_2$ is 2.432 and the molar polarization $_\infty P_2$ is 333 c.c.

In order to exhaust the possible methods of mathematical extrapolation to infinite dilution, the following method based on the volume polarization introduced by Van Arkel and Snoek [5] was attempted.

Starting from $p_2 = p_1 + \dfrac{1}{V_2}(p_{12} - p_1)$, where the volume polarization $p = \dfrac{\epsilon - 1}{\epsilon + 2}$, we assume $\epsilon = \epsilon_1(1 + aV_2)$. Substituting for $\epsilon$,

$$p_2 = p_1 + \frac{1}{V_2}\left[\frac{\epsilon_1(1 + aV_2) - 1}{\epsilon_1(1 + aV_2) + 2} - \frac{\epsilon_1 - 1}{\epsilon_1 + 2}\right]$$

$$p_2 = p_1 + \frac{1}{V_2} \cdot \frac{3a\epsilon_1 V_2}{(\epsilon_1 + 2)\{\epsilon_1(1 + aV_2) + 2\}}.$$

Proceeding to the limit when $V_2 \longrightarrow 0$

$$_\infty p_2 = p_1 + \frac{3a\epsilon_1}{(\epsilon_1 + 2)^2}.$$

It may be noted that this method reduces the mathematical calculations considerably. Taking the extrapolated value of $a\epsilon_1$, the polarization per c.c. $_\infty p_2 = 2.846$ and the molar polarization $_\alpha P_2 = 338$ c.c.

The Sugden relation $P_2 = A + B\dfrac{\epsilon - 1}{\epsilon + 2}$ applied to a solute in one particular solvent at one temperature is found to hold for all the solutions investigated. According to Sugden [6] $A = a + {}_{\text{ga}}P_2$ and $B = {}_{\text{gas}}P_0$. From the solutions investigated this part of Sugden's relation cannot be substantiated. The values of A are different for the same solute in different solvents, the extreme variation being 6%. This may be due to the variation of $a$ with the solvent. The slope B of the lines is not constant for the same solute in different solvents, the extreme variation being 11%. Similar variations of A and B have been noted by Jenkins.[7] Thus, while it is generally accepted that the Sugden relation is of the right form for a solute in one particular solvent at one temperature, " it is doubtful if the significance originally attached to A... and to B... can be substantiated either theoretically or from actual measurements." (Glasstone[8])

So far the Sugden relation has been used exclusively to calculate the polarization in the gaseous state. Taking advantage of the linearity of the relation it was thought desirable to use it to calculate the total molar polarization $(_\alpha P_2)$; this being the value of $P_2$ at $\dfrac{\epsilon_1 - 1}{\epsilon_1 + 2}$, where $\epsilon_1$ is the dielectric constant of the pure

solvent. Such a method has an obvious advantage over the usual method of curvilinear extrapolation using the $P_2$—$f_2$ curves. Since the relation is linear, $_\infty P_2$ can be calculated by mathematical computation using either the method of averages or least squares. $_\infty P_2$ calculated in this manner is given in table II. The values agree, wherever possible, with those obtained from graphical extrapolation and Hedestrand's method. On account of the mathematical procedure involved, the results obtained from the Sugden relation were used to calculate the electric moment.

TABLE II

*Polarisation at infinite dilution by different methods*

| | Hexane | Heptane | Carbon tetrachloride | Benzene | Toluene | Carbon disulphide | Chloroform |
|---|---|---|---|---|---|---|---|
| *o*-nitrotoluene | | | | | | | |
| Graphical | 342 | 363 | 334 | 330 | 319 | 295 | 224 |
| Hedestrand's | 343 | 365 | 333 | 333 | 316 | 293 | 225 |
| Sugden's | 346 | 354 | 334 | 330 | 317 | 302 | 224 |
| *m*-nitrotoluene | | | | | | | |
| Graphical | 429 | 441 | 395 | 411 | 385 | 375 | 266 |
| Hedestrand's | 417 | 432 | 391 | 418 | 389 | 372 | 261 |
| Sugden's | 420 | 428 | 404 | 412 | 388 | 365 | 264 |
| *p*-nitrotoluene | | | | | | | |
| Graphical | 493 | 503 | 442 | 452 | 443 | 415 | 306 |
| Hedestrand's | 484 | 473 | 435 | 462 | 444 | 408 | 298 |
| Sugden's | 486 | 469 | 443 | 454 | 434 | 412 | 302 |

For each of the solutions the electronic polarization $P_{E_2}$ was sensibly constant. Hence the relation $P_{E_2} f_2$—$f_2$ represents a straight line whose slope is $P_{E_2}$. $P_{E_2}$ was, therefore, calculated using least squares. The apparent electric moment was calculated from

$$\mu = 0.01273 \; \sqrt{(_\infty P_2 - P_{E_2}) \, T} \;\; \text{Debye.}$$

The values are given in table III.

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TABLE II

*Apparent electric moment of o-, m- and p-nitrotoluene*

| Solvent | ortho- | meta- | para- |
|---|---|---|---|
| Hexane | 3.91 | 4.33 | 4.68 |
| Heptane | 3.94 | 4.38 | 4 60 |
| Carbon tetrachloride | 3.81 | 4.23 | 4 45 |
| Benzene | 3.79 | 4.29 | 4.52 |
| Toluene | 3.71 | 4 12 | 4.41 |
| Carbon disulphide | 3.61 | 4.01 | 4.29 |
| Chloroform | 3.01 | 3.32 | 3 59 |

Applying Müller's empirical relation

$$\frac{P_0 \text{ (solution)}}{P_0 \text{ (gas)}} = 1 - 0.075 \; (\epsilon_{solvent} - 1)^2$$

to the data in hand the following results were obtained.

TABLE IV

*$P_0(gas)$ and $\mu(gas)$ calculated from Müller's relation*

| | ortho- | | meta- | | para- | |
|---|---|---|---|---|---|---|
| | $P_0$ (gas) | $\mu$ (gas) | $P_0$ (gas) | $\mu$ (gas) | $P_0$ (gas) | $\mu$ (gas) |
| Hexane | 330.1 | 4.03 | 405.4 | 4.46 | 474.4 | 4.83 |
| Heptane | 338.5 | 4.08 | 417.8 | 4 53 | 461.7 | 4.76 |
| Carbon tetrachloride | 332.7 | 4 04 | 410.2 | 4.49 | 454.0 | 4.72 |
| Benzene | 332.7 | 4.04 | 425.9 | 4.57 | 472.4 | 4.82 |
| Toluene | 324.9 | 4 00 | 406.1 | 4.47 | 459.6 | 4 75 |
| Carbon disulphide | 332.8 | 4.04 | 411.9 | 4.50 | 469.7 | 4.80 |

The agreement for all the solutes is fairly good.

The Sugden relation $_\alpha P_2 = A + B \frac{\epsilon - 1}{\epsilon + 2}$, as applied to one solute in different solvents, was next considered. According to Sugden, the extrapolated value of $_\alpha P_2$ at $\epsilon = 1$ should give the total polarization in the gaseous state augmented by a small constant, while the slope of the line should give the orientation

polarization in the gaseous state. The graph showing $_\infty P_2$ against $\dfrac{\epsilon-1}{\epsilon+2}$ represents a straight line. The values of the intercept A and the slope B of the lines are :

$$
\begin{aligned}
\text{ortho-nitrotoluene} \quad &\text{A } 454, \quad &-\text{ B } 420 \\
\text{meta-nitrotoluene} \quad &\text{A } 552, \quad &-\text{ B } 514 \\
\text{para-nitrotoluene} \quad &\text{A } 618, \quad &-\text{ B } 550
\end{aligned}
$$

Jenkins' relation $_\infty P_2 = K_1 + \dfrac{K_2}{\epsilon}$ was next considered. The graph showing $_\infty P_2$ against $\dfrac{1}{\epsilon}$ was found to indicate the expected straight line. When the line was extrapolated to $\epsilon = 1$, to obtain the polarization in the gaseous state, the intercept was found to be too high. At this stage it was thought desirable to exclude the results directly read off from the graphs. Jenkins' relation may be written as $_\infty P_2 \epsilon = K_1 \epsilon + K_2$. The constants $K_1$ and $K_2$ were calculated using the method of averages. The values obtained were :

$$
\begin{aligned}
\text{ortho-nitrotoluene} \quad &K_1 \ 140, \quad K_2 \ 416, \quad K_1 + K_2 \ 556 \\
\text{meta-nitrotoluene} \quad &K_1 \ 157, \quad K_2 \ 535, \quad K_1 + K_2 \ 692 \\
\text{para-nitrotoluene} \quad &K_1 \ 193, \quad K_2 \ 558, \quad K_1 + K_2 \ 751
\end{aligned}
$$

$K_1 + K_2$ given in the last column represents the value of the polarization in the gaseous state $(\epsilon = 1)$.

Failing to get any correspondence between the values derived from the empirical relations of Müller, Sugden and Jenkins, it was thought desirable to investigate the relation between the polarization at infinite dilution $_\infty P_2$ and the dielectric constant $\epsilon$ of the solvent. It may be assumed that $_\infty P_2$ and $\epsilon$ are connected by a relation $_\infty P_2 = a\epsilon^{b}$.

Hence $\log {_\infty P_2} = \log a + b \log \epsilon$.

The plot of $\log {_\infty P_2}$ against $\log \epsilon$ for solution in different solvents showed three parallel lines with an approximate slope $-0.5$. This furnishes an indication that the relation is the same for all the solutes. The graphical methods, however, are subject to personal error ; hence the slope and the intercept were evaluated using least squares. This method has a further advantage ; the correlation coefficient provides a test for the linearity of the relation which is assumed. The results are :

| Solute | Intercept *a* | Slope *b* | Correlation co-efficient |
|---|---|---|---|
| *o*-nitrotoluene | 487 | −0.4928 | 1−0.004 |
| *m*-nitrotoluene | 608 | −0.5256 | 1−0.01 |
| *p*-nitrotoluene | 666 | −0.5012 | 1−0.004 |

Thus for the substances investigated $_{\infty}P_2 = \dfrac{a}{\sqrt{\epsilon_{solvent}}}$

when $\epsilon = 1$, $_{\infty}P_2 = a$; and this may be regarded as the value for the gaseous state.

So far as the empirical relations are concerned it may be concluded that: (*i*) of the four empirical relations considered, Müller's relation gives the best agreement; (*ii*) the relations of Sugden, Jenkins and the authors are suitable to represent the results; (*iii*) extrapolation to $\epsilon = 1$ gives widely different values in the three instances where it is used. At this stage it is felt that there is good reason to suspect the validity of extrapolation to $\epsilon = 1$ for the gaseous state. The empirical relations have been derived from results obtained from measurements on solutions and as such must apply only so far as the liquid state is concerned. The region beyond the point representing the pure solvent is unexperimented on and to that extent unknown; there is no evidence to assume that the prolongation of the graphs in that region is valid.

Frank's relation $\dfrac{\mu(\text{sol.})}{\mu(\text{gas})} = 1 + (A_1 + A_2) - \dfrac{A_1 + A_2}{\epsilon}$ was then considered. The equation may be written in the form $\mu(\text{sol.}) = a + b/\epsilon$. The constants $a$ and $b$ were calculated applying the method of averages. Knowing these, the moment in the vapour state ($\epsilon = 1$) was calculated.

| | | |
|---|---|---|
| *o*-nitrotoluene | $\mu(\text{gas})$ | 5.31 |
| *m*-nitrotoluene | $\mu(\text{gas})$ | 6.00 |
| *p*-nitrotoluene | $\mu(\text{gas})$ | 6.17 |

These values are very high compared with those derived from Müller's relation. It may, however, be remarked that Frank's equation usually gives a high value on extrapolation to $\epsilon = 1$.

The applicability of Higasi's theories was next considered. In the absence of the values of the optical polarizabilities of ortho-, meta- and para-nitrotoluene, the size of the molecule was ascertained from X-ray data. It is now fairly well established that the benzene nucleus is similar, both in structure and in dimensions, to the plane ring of six carbon atoms, each of diameter 1.41 Å, previously known to exist in graphite.

Starting from this plane model, the dimensions of the molecules of ortho-, meta- and para-nitrotoluene were calculated taking the necessary data from Robertson[9] and James, King and Horrocks.[10] The electric moment might be taken to act along the diameter of the regular hexagon joining the centres of the C-atoms of the benzene ring. Since the moment of $-NO_2$ is $-3.8$ and of $-CH_3$ 0.4 (Williams[11]) it may be assumed that while locating the dipole only $-NO_2$ need be considered. Higasi[12] has assumed the dipole to be at the centre for the nitrobenzene molecule. Hence it was assumed that the dipole in ortho-, meta- and para-nitrotoluene is also at the centre of the molecule. Taking $a$ to represent

the length along the dipole axis and $b$ to represent the width of the molecule, the ratio $a/b = K$ was calculated from the X-ray data. Thus

| | | | | |
|---|---|---|---|---|
| $o$-nitrotoluene | $a$ 6.23, | $b$ 4.98, | K 1 251, | A $-0.059$ |
| $m$-nitrotoluene | $a$ 6.23, | $b$ 4.98, | K 1.251, | A $-0.059$ |
| $p$-nitrotoluene | $a$ 7.70, | $b$ 4.23, | K 1.42, | A $-0.142$ |

Since K is greater than unity in each case, the value of A was calculated from

$$A = \frac{-1}{K^2 - 1} \left\{ 1 - \frac{K}{\sqrt{K^2 - 1}} \log (K + \sqrt{K^2 - 1}) \right\} - \frac{1}{3}.$$ Using these values of A, $\mu$(gas) was calculated from

$$\mu(\text{gas}) = \frac{\mu \text{ (sol)}}{1 + 3 \frac{\varepsilon - 1}{\varepsilon + 2} A}.$$

| Solvent | Ortho- | Meta- | Para- |
|---|---|---|---|
| Hexane | 4·07 | 4·51 | 5·18 |
| Heptane | 4·11 | 4·57 | 5.12 |
| Carbon tetrachloride | 4·01 | 4·46 | 5·07 |
| Benzene | 4·00 | 4·53 | 5·17 |
| Toluene | 3·93 | 4·36 | 5·09 |
| Carbon disulphide | 3·85 | 4·28 | 5·05 |
| Chloroform | 3·34 | 3·68 | 4·71 |

The values calculated from Higasi's equations show a slight agreement with those derived from Müller's relation for ortho- and meta-nitrotoluene. For para-nitrotoluene the agreement is not good. Besides, the results for solution in chloroform do not fit into the set. Assuming that this difference is due to fixing the dipole at the centre of the molecule, instead of locating it at the contact of C and N atoms, the result for para-nitrotoluene was recalculated using $A = B_1 + A_2$.

$$B_1 = \frac{-c^2}{a_1^2 - c^2} \left\{ 1 - \frac{a_1}{\sqrt{c^2 - a_1^2}} \sin^{-1} \frac{\sqrt{c^2 - a_1^2}}{c} \right\} - \frac{1}{3}$$

$$A_2 = \frac{-c^2}{a_2^2 - c^2} \left\{ 1 - \frac{a_2}{\sqrt{a_2^2 - c^2}} \log \frac{a_2 + \sqrt{a_2^2 - c^2}}{c} \right\} - \frac{1}{3}$$

$a_1 = 1.99$, $a_2 = 5.71$, $c = 2.11$ were calculated from X-ray data.

Recalculating $\mu$(gas) for para-nitrotoluene the following result was obtained.

| Solvent | $\mu$(gas) |
|---|---|
| Hexane | 5·32 |
| Heptane | 5·27 |
| Carbon tetrachloride | 5·25 |
| Benzene | 5·36 |
| Toluene | 5·28 |
| Carbon disulphide | 5·28 |
| Chloroform | 5·10 |

There is good agreement between the values for different solvents if we assume the dipole to be at the contact of C and N atoms; on the other hand, the difference between $\mu$(gas) from Higasi's equation and from Müller's relation has increased. It is difficult to choose between the two sets of values since each set shows good inter-agreement and there is no extraneous determination of the moment in the gaseous state. It may, then, be concluded that while Higasi's equation gives in some cases values nearly the same as those given by Müller's relation, it is reduced to an approximation when the dimensions of the molecule are not known. Besides, exact location of the dipole in the molecule is uncertain in many cases, and to that extent are uncertain the results obtained from Higasi's theory.

It seems apparent that no agreement is possible between gas $P_2$ derived from different empirical relations so long as extrapolation is carried out to $\epsilon = 1$ for the gaseous state. The validity of extrapolation to $\epsilon = 1$ has already been questioned. Marsden and Moss[13] have shown that the dielectric constant of liquids and their saturated vapour are not identical at the critical temperature. In view of this discontinuity in the dielectric constant it seems reasonable to carry out extrapolation only up to transition from the liquid to the gaseous state.

Le Fèvre[14] has found that the dielectric constant of benzene, carbon tetrachloride, carbon disulphide and other liquids is nearly the same at the critical temperature of the respective liquids. This may be called the critical dielectric constant. Since the polarization of a non-polar substance does not vary with temperature, the critical dielectric constant can be calculated from

$$\frac{\epsilon_c - 1}{\epsilon_c + 2} \cdot \frac{1}{d_c} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{d} \, ,$$

where the sub-index $c$ denotes the values at critical temperature. The transition dielectric constant at temperature $t°C$ may be calculated from

$\epsilon_t = \epsilon_c + \dfrac{d\epsilon}{dt}(t - T_c)$. The transition dielectric canstant works out to be 1.60 for hexane, 1.64 for heptane, 1.81 for carbon tetrachloride and 1.86 for benzene at 30°C. Hence for one solute in different solvents extrapolation may be carried out to $\epsilon = 1.7$, (the mean).

When the relations of Sugden, Jenkins and the authors are each extrapolated to $\epsilon = 1.7$, there is a general unification in the values obtained from the different relations.

| Substance | Müller c.c | Sugden c.c. | Authors c.c. | Jenkins c.c. |
|---|---|---|---|---|
| o-nitrotoluene | 369 | 368 | 374 | 385 |
| m-nitrotoluene | 451 | 466 | 466 | 472 |
| p-nitrotoluene | 503 | 513 | 511 | 521 |

Table V gives the value of the electric moment in the gaseous state of ortho-, meta- and para-nitrotoluene as obtained from different methods. The values marked with asterisks are calculated using extrapolation to $\epsilon = 1.7$. The mean value of the moment in different solvents is taken for Müller's relation. The same is done for the values derived from Higasi's equation but the polar solvent chloroform is not taken into account.

TABLE V

|  | *o*-nitrotoluene | *m*-nitrotoluene | *p*-nitrotoluene |
|---|---|---|---|
| Müller | 4.04 | 4.51 | 4.78 |
| Sugden* | 4.03 | 4.53 | 4.84 |
| Authors* | 4.07 | 4.58 | 4.82 |
| Jenkins* | 4.13 | 4.62 | 4.87 |
| Frank* | 4.15 | 4.64 | 4.86 |
| Higasi | 4.00 | 4.45 | 5.11 |

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