

DIELECTRIC BEHAVIOR OF SOME NON-POLAR MOLECULES

by

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ABSTRACT

Dielectric behavior of tin tetraiodide was investigated by the senior author by determining the dielectric constants of its carbon tetrachloride solutions by use of a Q-meter last year. In order to obtain more accurate results, a very precision equipment, impedance bridge, was applied to investigate it again.

In this investigation, the experiment consists of:

1. Purification of carbon tetrochloride;
2. Synthesis and purification of tin tetraiodide;
3. Preparation of sample solutions;
4. Capacitance measurements;
5. Dipole moment calculation.

The calculated result of dipole moment of SnI_4 is so small that the structure of its molecule is predicted to be non-polar.

INTRODUCTION

Dielectric behavior of tin tetraiodide was investigated by measuring the dielectric constants of its carbon tetrachloride solutions by the senior author by use of an equipment, Q-meter, last year [1]. For some reason, the number of significant figures in the data of those experiments did not meet the proper requirements. Therefore, further accurate measurements have been put into practice by use of a more precision equipment, impedance bridge, this year.

The differences between the two equipments are:

1. Q-meter is an equipment of resonance type circuit. The frequency of the applied field of it was fixed at 2 mc. whereas that of the impedance bridge is 1 kc. As the loss factor (ϵ'') is very small when the frequency of applied field is low [2], the latter equipment must give the better results.
2. The capacitor used last year was a parallel pair of aluminum sheets. The capacity of it was low and fixed. In this year, a 400 μmf variable precision capacitor was used. And the solution used in every measurement was 100 ml instead of 50 ml used last year.

The reading of the variable condenser in each measurement was obtained by taking the difference of two capacities, one in air and one in solution. It is capable to give quite accurate results [3].

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THEORETICAL

When a diatomic or polyatomic molecule has atoms with different electronegativity, the centers of positive and negative charges do not coincide in one point, i. e., there is a distance between the two centers. The molecule is then called to have a dipole which is a pair of electric charges, equal in size, opposite in sign, and very close together. The size of the dipole moment is the product of either charge q by the distance r between them, that is $\mu = qr$.

If a molecule has atoms with the same electronegativity, or with different electronegativity but with symmetrical atomic arrangement, the centers of negative and positive charges coincide in one point. i. e., $r=0$, then $\mu=0$. In this case, the dipole moment is said to be zero.

In case the molecule of any substance has zero dipole moment, the orientation polarization P_μ is zero. Hence the distortion or deformation polarization P_D , which is the sum of the electron polarization P_E and the atomic polarization P_A , is equal to the total molar polarization P since the total molar polarization is given by

$$P = P_A + P_E + P_\mu = P_D + P_\mu \quad (1)$$

The total molar polarization is calculated by measuring dielectric constants of dilute solutions with non-polar solvents at frequency of radio range or audio range.

Because tin tetraiodide is easy to be decomposed by heating and the dielectric constant measurement at frequency higher to infrared and visible range is difficult, therefore, the distortion polarization P_D can not be determined by temperature method or by direct measuring dielectric constant at frequency of infrared and visible range. However, P_D can be calculated by Lorenz-Lorentz equation

$$P_D = P_A + P_E = \frac{4\pi N}{3} \alpha_D = \frac{n^2 - 1}{n^2 + 2} \frac{M}{d} = R \quad (2)$$

where

N = Avogadro's number,

α_D = distortion polarizability,

n = refractive index of dielectric,

M = molecular weight of dielectric,

d = density of dielectric,

R = molar refraction of dielectric.

The polarization of solutions, P_{12} , is calculated by use of the modified Clausius-Mosotti-Debye equation applicable to solutions:

$$\frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \frac{f_1 M_1 + f_2 M_2}{d_{12}} = \frac{4\pi N}{3} (f_1 \alpha_1 + f_2 \alpha_2) = f_1 P_1 + f_2 P_2 = P_{12} \quad (3)$$

where

ϵ_{12} = dielectric constant of solution,

f_1, f_2 = mole fractions of solvent and solute,

M_1, M_2 = molecular weights of solvent and solute,

d_{12} = density of solution,

α_1, α_2 = polarizabilities of solvent and solute in solution,

P_1, P_2 = total molar polarizations of solvent and solute in solution,

P_{12} = molar polarization of solution.

In the above equation, ϵ_{12} , f_1 , d_{12} can be measured directly or calculated indirectly P_1 is calculated by Clausius-Mosotti equation

$$P_1 = \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \frac{M_{11}}{d_1}, \quad (4)$$

in which P_1 is used as P°_1 , the total molar polarization of pure solvent, and ϵ_1 and d_1 are the dielectric constant and density of pure solvent respectively. The quantities ϵ_1 and d_1 can be obtained from handbooks or calculated from the following two equations:

$$\begin{aligned} \epsilon_{12} &= \epsilon_1 + a f_2 \\ d_{12} &= d_1 + b f_2 \end{aligned} \quad (5)$$

By plotting curves of ϵ_{12} and d_{12} against f_2 , the intercepts ϵ_1 and d_1 can be found at $f_2=0$ respectively.

P_2 is calculated from the following relation:

$$P_2 = \frac{P_{12} - P_1}{f_2} + P_1$$

or

$$P_{12} = P_1 + (P_2 - P_1) f_2 \quad (6)$$

By plotting P_{12} against f_2 , P_1 is the intercept of the curve, and $(P_2 - P_1)$ is the slope of the line. By adding the value of the intercept to the value of the slope, P_2 is obtained. It is used as P°_2 , also $P_{2\infty}$.

P_2 can also be calculated by the equation derived by Halverstadt and Kumler from Onsager's equation [2]:

$$P_{2\infty} = \frac{3\alpha v_1 M_2}{(\epsilon_1 + 2)^2} + M_2 (v_1 + \beta) \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \quad (7)$$

where

$$v_1 = 1/d_1 = \text{specific volume of solvent,}$$

$$v_{12} = 1/d_{12} = \text{specific volume of solution,}$$

$$\alpha, \beta = \text{slopes of the two lines of the following two equations:}$$

$$v_{12} = \epsilon_1 + \alpha w_2 \quad (8)$$

$$v_{12} = v_1 + \beta w_2$$

in which w_2 is the weight fraction of solute and v_{12} is the specific volume of solution. The above two equations are derived from Onsager's equation by the fact that dielectric constant is proportional to the number of molecules of solute per c. c., which in turn is proportional to the weight fraction of the solute in the dilute solution.

$P_{2\infty}$ is then used as P°_2 , the total molar polarization of pure solute, i. e.,

$$P^{\circ}_2 = P_{2\infty} = P^{\circ}_{2A} + P^{\circ}_{2E} + P^{\circ}_{2\infty} \quad (9)$$

$$P^{\circ}_2 = P_{2\infty} - (P^{\circ}_{2A} + P^{\circ}_{2E})$$

and the dipole moment can be calculated by Debye equation:

$$P^{\circ}_2 = \frac{4\pi N^2 \mu^2}{9KT} \quad (10)$$

$$= \left(\frac{P^{\circ}_{2\infty} 9kT}{4\pi N} \right)^{\frac{1}{2}} \quad (11)$$

$$= 0.01282 \times 10^{-18} (P^{\circ}_{2\infty} T)^{\frac{1}{2}} \text{ e. s. u. cm.}$$

$$= 0.01282 \times (P^{\circ}_{2\infty} T)^{\frac{1}{2}} D$$

where D is Debye unit, T is the absolute temperature.

EXPERIMENTAL

Equipments and apparatus:

1. All dielectric measurements were carried out by use of a universal impedance bridge (Electro-measurements Inc., model 291, $c=0-1200$ microfarads in 7 ranges, $0-1200$ f on the lowest range, $0.1\mu\text{f}$ per dial division, accuracy $\pm (0.2\%+1$ dial division), $D=0-10.5\times f_{kc}$ in 3 ranges, $0,001\times f_{kc}$ per dial division on the lowest D range, accuracy $\pm (2\%+0.04 f_{kc})$. (Figure 1)

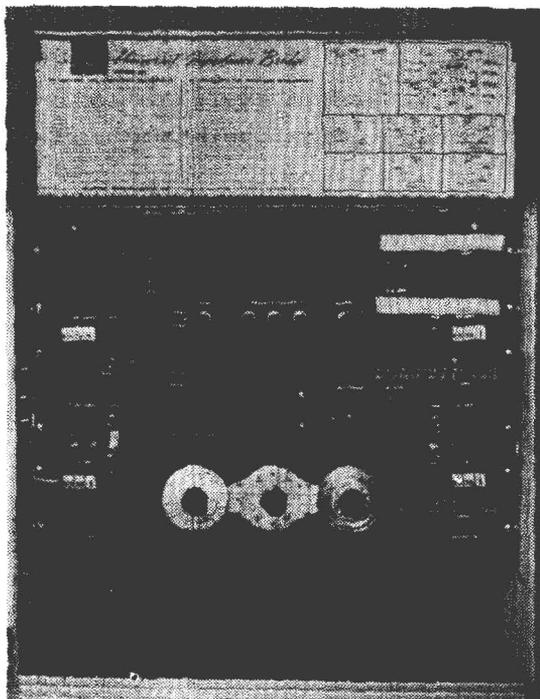


Fig 1. Impedance bridge

2. A $400\mu\text{f}$ variable precision capacitor was used to measure the capacitance.
3. Fractionating apparatus, reflux condenser, drying apparatus, melting point apparatus (all made in Shing Tong Co., Inc., Taiwan) were used throughout the experiments.

Preparation of materials and reagents:

1. Purification of CCl_4 :

Carbon tetrachloride was purified by A. Weissberger and E. Proskauer method [4]. It was washed with warm potassium hydroxide solution at $50-60^\circ\text{C}$ for three times to remove carbon disulfide and the acidic impurities, then washed with distilled water and dried over anhydrous calcium chloride for days, and then distilled just before using. The portion to be collected was collected at 76.8°C .

2. Synthesis and purification of SnI_4 :

Tin tetraiodide was prepared by Therald Moeller method [5] and purified by M. E. Dorfman method [6]. Pure iodine and excess pure tin were refluxed in

pure carbon tetrachloride for 6~8 hours until the color of the solution changed from violet to orange red and the violet vapor above the solution disappeared, i. e., the reaction $\text{Sn (excess)} + 2\text{I}_2 \rightarrow \text{SnI}_4$ is completed. The hot tetraiodide solution was filtered with steam jacketed funnel. Then it was recrystallized in carbon tetrachloride for five times, and dried under 120°C for 14 hours. The melting point of synthetic and purified tin tetraiodide was measured as 143.5 to 144.1°C .

3. Dilute solutions of SnI_4 in CCl_4 :

Eight solutions were prepared by dissolving 0.45480 g, 0.99205 g, 1.49770 g, 1.99485 g, 2.49170 g, 2.9048000 g, 4.00100 g, 4.93620 g, purified SnI_4 in eight 100 ml purified CCl_4 respectively. Solutions were weighed directly by use of pycnometers in order to diminish the possible errors. The density of each solution was measured by weighing pure water of the same volume in the same volumetric flask.

Dielectric constant measurements:

Dielectric constants of solutions (ϵ_{12}) were measured by using an impedance bridge, connecting with a $400\mu\text{mf}$ variable precision capacitor. The dielectric constants of the prepared solutions were obtained by dividing the difference in capacitance between two positions b and a, while the plates of the capacitor, being closed and completely opened, immersed in the liquid, by the corresponding difference with air as the dielectric, that is

$$\epsilon_{12} = \frac{C_{b, \text{sol'n}} - C_{a, \text{sol'n}}}{C_{b, \text{air}} - C_{a, \text{air}}}$$

CALCULATION

Table 1 gives the experimentally determined dielectric constants and densities of the solutions at 29°C together with the values of the polarization P_{12} calculated by means of equation (3) .

Table 1 (T=302° K)

<u>Specimen</u>	<u>ϵ_{12}</u>	<u>$d_{12}(\text{g/cc})$</u>	<u>$f_1 \times 10$</u>	<u>$f_2 \times 10^8$</u>	<u>$P_{12}(\text{cc})$</u>
1	2.223	1.5808	9.9929	0.70827	28.244
2	2.225	1.5855	9.9846	1.5429	28.264
3	2.224	1.5849	9.9767	2.3345	28.329
4	2.227	1.5858	9.9689	3.1091	28.363
5	2.231	1.5895	9.9618	3.8242	28.557
6	2.229	1.6026	9.9550	4.5045	28.232
7	2.236	1.6047	9.9374	6.2552	28.550
8	2.349	1.6072	9.9229	7.7080	30.393
<u>$d_1(\text{g/cc})$</u>	<u>ϵ_1</u>	<u>a</u>	<u>b</u>	<u>$M_1(\text{m. wt. CCl}_4)$</u>	
1.5778	2.221	2.266	3.707	153.84	

Curves showing the variation of these quantities with the composition of the solution are plotted in Figures 2, 3. The intercepts of the two curves at $f_1=0$ in

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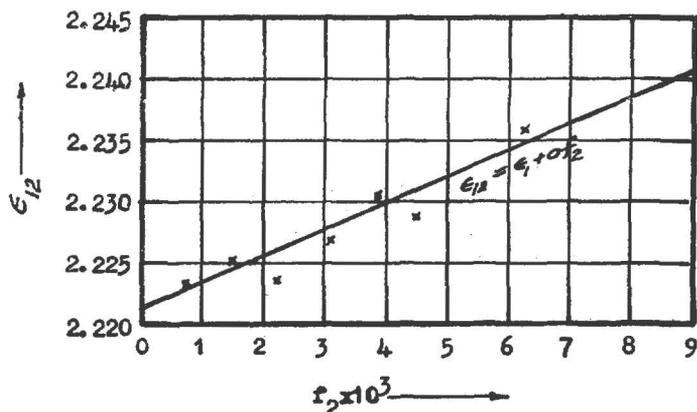


Fig 2. Graph of ϵ_{12} against f_2 .

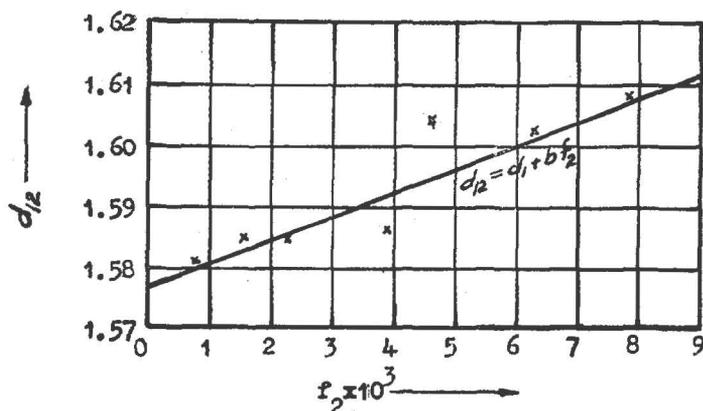


Fig 3. Graph of d_{12} against f_2 .

Figures 2, 3 are ϵ_1 and d_1 respectively. They are taken to replace the values of dielectric constant and density of pure solvent CCl_4 which can be found in handbooks. By substituting the values of ϵ_1 and d_1 into equation (4), the molar polarization, P_1 , of solvent in solution is obtained. Because the solutions are very dilute, P_1 is taken to replace P_1^0 , molar polarization of pure solvent. The value of P_1 is found to be 28.204 (cc). It is noted that the experimental value of P_1 agrees very closely with the above value (see Figure 6).

Since the solutions are extremely dilute, P_2 is most significant in equation (6). The difference $P_{12} - P_1$ is so small that the effect of any error in P_{12} will become tremendous when dividing by the very small quantity f_2 . Therefore, from $P_2 - f_2$ curve, when $f_2 = 0$ the extrapolated value of $P_{2\infty}$ is not significant. Hence equation (7) derived by Halverstadt and Kumler is used to calculate $P_{2\infty}$. In the said equation, α and β are the slopes of the curves of equations (8), whereas ϵ_1 and v_1 are the intercepts of these same two equations (Figure 4, 5). Table 2 gives the experimental and calculated values and extrapolated values of the corresponding quantities.

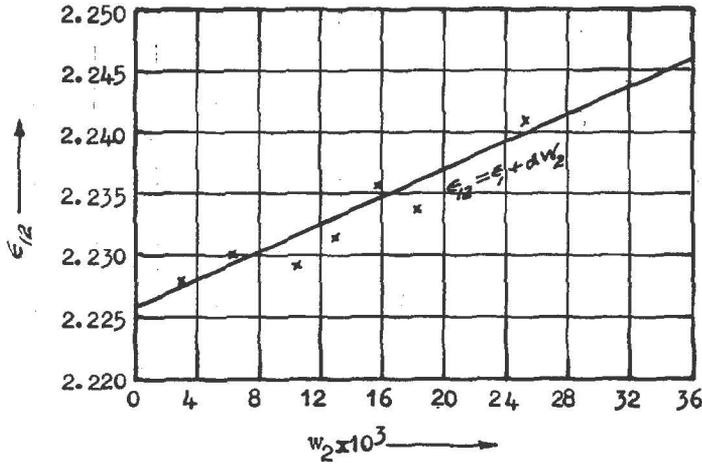


Fig. 4. Graph of ϵ_{12} against w_2 .

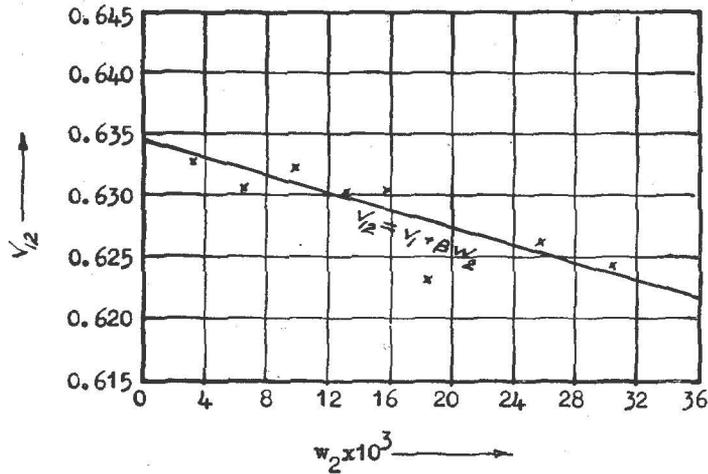


Fig. 5. Graph of v_{12} against w_2 .

Table 2 ($T=302^\circ\text{K}$)

Specimen	$w_2 \times 10^3$	α	v_1	β	$P_2^0 D$ (cc)
1	2.877	0.5709	0.6345	-0.4286	74.964
2	6.252				
3	9.459				
4	12.588				
5	15.743	$\frac{P_2 - P_1}{(cc)}$	$\frac{P_1}{(cc)}$	$\frac{P_2}{(cc)}$	$\frac{P_3}{(cc)}$
6	18.090	48.125	28.220	76.345	75.507 (semi-mathematically)
7	24.967				76.345 (semi-graphically)
8	30.654				75.926 (mean)

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In order to check the value of P_{2s} obtained above, the second of equation (6) was used to plot P_{12} against f_2 , as Figure 6. The sum of the intercept at $f_2 = 0$ and the slope of the line is P_{2s} . Hence, it is found that $P_2 = 76.345$ cc.

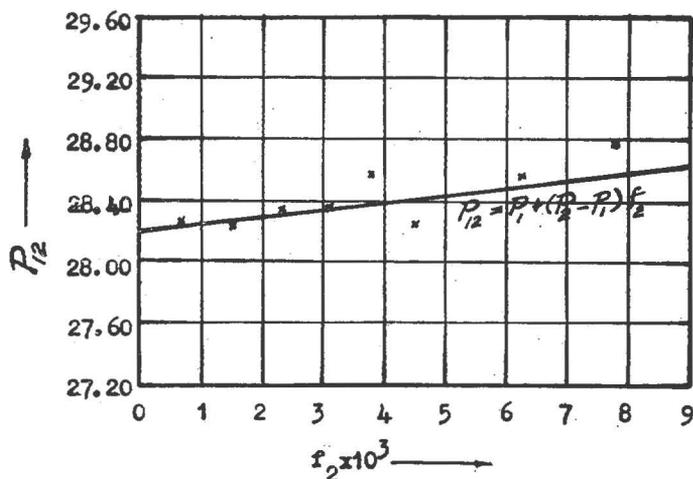


Fig 6. Graph of P_{12} against f_2 .

P_{2s} then is used as P°_2 , the total molar polarization of pure solute tin tetraiodide. This value is very close to the value P°_{2D} calculated from Lorentz-Lorenz equation [2, 7].

$$P^{\circ}_{2D} = P^{\circ}_{2A} + P^{\circ}_{2E} = \frac{n^2 - 1}{n^2 + 2} \frac{M_2}{d_2} = 74.7 \text{ (cc)}$$

where $n=2.106$, the refractive index of tin tetraiodide for sodium D line [8];

$M_2=626.34$, molecular weight of tin tetraiodide;

$d_2=4.46$, density of tin tetraiodide [8];

P°_{2D} =distortion polarization of pure tin tetraiodide;

P°_{2A} =atomic polarization of pure tin tetraiodide;

P°_{2E} =electron polarization of pure tin tetraiodide.

Since
$$P^{\circ}_2 = P^{\circ}_{2D} + P^{\circ}_{2\mu} = \frac{4}{3} \pi N \alpha_D + \frac{4}{3} \pi N \frac{\mu^2}{3kT}$$

so that
$$P^{\circ}_{2\mu} = \frac{4}{3} \pi N \frac{\mu^2}{3kT} = \frac{4 \pi N \mu^2}{9 kT}$$

Therefore
$$\begin{aligned} \mu &= 0.01292 \times 10^{-18} \sqrt{P^{\circ}_{2\mu} T} \text{ esu cm} \\ &= 0.01282 \times 10^{-18} \sqrt{(P^{\circ}_2 - P^{\circ}_{2D}) T} \text{ esu cm} \\ &= 0.01282 \times 10^{-18} \sqrt{(75.926 - 74.964) 302.16} \text{ esu cm} \\ &= 0.2185 \text{ D} \end{aligned}$$

DISCUSSION AND CONCLUSION

The value of dipole moment of SnI_4 obtained by the present investigation is only 0.2185 D (it was 0.231 D last year). It is so slightly different from zero that the authors believe that if the degree of accuracy of the measuring instruments is further improved, a nearly zero dipole moment can be expected. Therefore, in the authors' opinion, the molecules of tin tetraiodide are non-polar and having a symmetrical tetrahedral structure with $\bar{4}3m$ (Td) symmetry [9].

As mentioned before, the densities of solutions were determined by use of 100 ml calibrated volumetric flask instead of small capacity pycnometer, and the measuring cell for dielectric constant determination was 100 ml instead of the 50 ml used last year and instead of 8 ml or 20 ml ones [10, 11, 12] which often used by others. Furthermore, the capacitor used this year was a 400 $\mu\mu\text{f}$ variable precision capacitor. These might compensate more or less the errors caused by inaccuracy of instruments, and hence a nearly zero dipole moment is still obtained.

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BIBLIOGRAPHY

1. L. Kao: "Dielectric behavior of tin tetraiodide", presented at the 1961 Annual Meeting of the Chinese Chemical Society, September, 1961.
2. C. P. Smyth, Dielectric Behavior and Structure, McGraw-Hill Book Co., Inc., (1955), pp. 224, 403.
3. Daniels, etc., Experimental Physical Chemistry, 5th edition (1956), McGraw-Hill Co. Inc., pp. 206~213.
4. A. Weissberger and E. Proskauer, Organic Solvent, Physical Constants and Methods of Purification, (1955), pp. 103, 105, 163.
5. J. C. Bailar, Inorganic Syntheses, vol. IV, McGraw-Hill Co. (1953), pp. 119~121.
6. M. E. Dorfman and J. H. Hildebrand, J. Am. Chem. Soc., 49, 729 (1927).
7. Kortum-Rockins, Electrochemistry, Elsevier Pub. Co. (1951), p. 553.
8. Lange, Hand Book of Chemistry, 8th edition (1952), pp. 294, 295.
9. P. J. Wheatley, The Determination of Molecular Structure (1958), p. 215.
10. A. R. Tourky and H. A. Rizk, J. Phy. Chem., 61, 231 (1957).
11. J. W. Williams and R. J. Allgeier, J. Am. Chem. Soc., 49, 2416 (1927).
12. J. G. Miller, *ibid.*, 56, 2360 (1934).

非極性分子之介電行為

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四碘化錫之分子結構，前曾由本文第一作者用 Q 計測定其四氯化碳溶液之介電常數以探研之。因欲獲更理想之結果，今復以更精確之儀器總阻抗電橋重作測定，以計算四碘化錫之偶極矩。全部實驗包括：

1. 溶劑四氯化碳之精製。
2. 四碘化錫之綜合及精製。
3. 樣品溶液之配製及密度測定。
4. 電容之測定及介電常數之計算。
5. 偶極矩之計算。

計算結果，四碘化錫之偶極矩與零值極為接近，其分子結構應屬非極性。

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