# The Dielectric Polarisation of Liquid Mixtures.

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*Introduction.*

The molecular polarisation of a substance in which the molecules are free to assume a perfectly random orientation can be expressed by the equation $P = \frac{\epsilon-1}{\epsilon+2} \cdot \frac{M}{\rho}$ where $\epsilon$ is the dielectric constant of the substance, M its molecular weight and $\rho$ its density. Debye theory[1] introduces the molecular polarisation in the form $P = A + \frac{B}{T}$ where A and B are two constants for the dielectric; A is equal to molecular refraction $\frac{n^2-1}{n^2+2} \cdot \frac{M}{\rho}$ extrapolated to infinite wavelength and B is equal to $\frac{4\pi N}{9K}\mu^2$ in which N=Avogadro number, K=Boltzmann gas constant and $\mu$=permanent electric moment of a single molecule forming a doublet. A includes the polarisation due to electric shifts induced in the molecule while B includes the polarisation due to doublet orientation caused by external field. In

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[1] Marx, Handbuch der Radiologie, 6, 614-619 (1925).

the case of gases the molecules are most free to move and experimental investigations [1] show that the expression $P = A + \frac{B}{T}$ represents admirably the temperature variation of dielectric constants of dipole gases. In the case of solids, however, the molecules are rigidly bound and therefore unable to orient themselves in an applied field with the result that B vanishes in this case. But as A, the extrapolated value of molecular refraction, does not account for the polarisation due to shifts of atoms or radicals induced in the molecules, P does not equal A. Errara [2] has indeed found out the polarisation P of a number of substances in the solid state showing that P differs from A calculated from optical data by definite constants depending on their infra-red frequencies. Thus $P - A$ is constant for solids, whereas it is an inverse function of temperature in the case of gases. But in the case of liquids, the molecules are neither rigidly bound nor perfectly free and thus $P - A$ becomes an odd function of temperatures which the simple theory is quite inadequate to explain. In the case of alcohols, [3] the curves of P versus $\frac{1}{T}$ give a negative slope suggesting an imaginary moment of the molecule. The failure of Debye theory in the case of polar liquids is generally attributed to association between molecules themselves. This association is presumably a function of concentration and temperature of the liquid. The effect of such association is generally to form molecular complexes so as to diminish the average effective moment just as in grouping of line magnets in ordinary iron pieces. To study the changes of association, the usual method is to dissolve the polar liquid in a non-polar solvent and find the molecular polarisation of the solution at different concentrations and temperatures. P is calculated

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[1] Zahn, Phys. Rev., 24, 400 (1924). Jona, Physik, Z., 20, 14 (1919). Smyth and Zahn, Journ Am. Chem. Soc., 47, 2501 (1925). [Sanger, Physik, Z., 27, 556, (1926), 28, 455 (1927).

[2] Errara, Physik, Z., 27, 764 (1926).

[3] Marx, Handbuch der Radiologie, 6. 680 (1925).

from the equation $M = M_1C_1 + M_2C_2$ where $M_1$, $M_2$ are molecular weight and $C_1$, $C_2$ are the molecular fraction concentrations of the solvent and the solute respectively. If the polarisation of the solvent and the solute be denoted by $P_1$ and $P_2$, $P$ can be expressed as $P_1C_1 + P_2C_2$ in which $P_1$ is constant for the nonpolar solvent. Thus $P_2$ can be calculated from the

expression $\frac{\epsilon-1}{\epsilon+2} \cdot \frac{M_1C_1 + M_2C_2}{\rho} = P_1C_1 + P_2C_2$ and plotted against con-

centration $C_2$ in a curve which would reveal the nature of association in the liquid. Investigations[1] in this direction clearly point out that the effect of association markedly diminishes with the lowering of concentration, and Debye has suggested that the zero-concentration intercepts of such curves would give the molecular polarisation of the solute in the unassociated state. This is based upon the assumption that the association vanishes towards zero concentration. It may therefore, be conjectured that Debye theory might hold for these extrapolated values of $P_2$ at different temperatures. To test the theory, data for low concentrations must be numerous and reliable so as to give well-defined intercepts and measurements should be carried on at several temperatures, but unfortunately few liquids have been tested from this stand-point. The present work is undertaken to study the nature of association in the case of some simple substituted benzene compounds, to check the zero-concentration intercepts against Debye theory and to find out the moments of the liquids. From its spherical structure, carbon-tetrachloride seems to be the most nonpolar substance, so that this liquid was taken as the solvent and measurements were carried out mostly with low concentration and at several temperatures.

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[1] Marx, Handbuch der Radiologie, 6, 630 (1935).
L. Lange, Zeits. f. Physik, 33, 169-183 (1925).
Smyth and Morgan, Journ. Am. Chem. Soc., 50, 1547 (1928).

*Experimental Procedure.*[1]

The dielectric constant of the mixtures was measured by a Heterodyne arrangement usually adopted for measurements on gases.[2] The method is too sensitive for the present purpose, but for low concentration $P-P_1C_1$ is very small and a slight error in the dielectric constant becomes enormously magnified in the process of calculation, so that this necessitates a very accurate determination of dielectric constant at low concentrations. The apparatus consisted of two similar reaction circuits A and B (fig. 1) oscillating with high frequency.
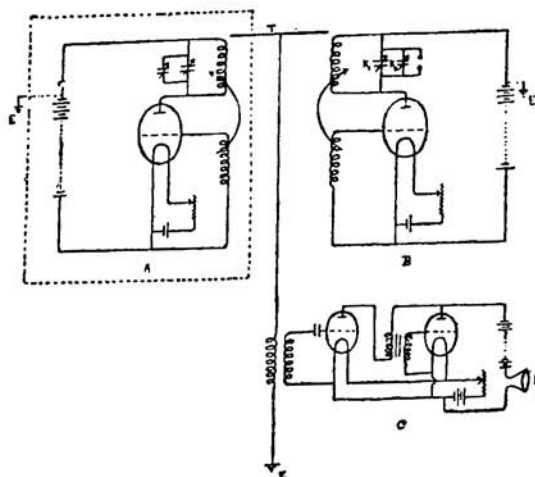


Fig. 1—Diagram of apparatus.

The oscillating valves were of Mullard P. M 4 type operated with 100 volts on the plate and 4 volts on the filament current of 12 amperes and a plate current of about

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[1] The experimental procedure was exactly the same as described in a paper on " The dielectric constant of nitrobenzene " by Mr. N. N. Pal of this laboratory. This has recently been sent for publication, and the details are given here only because that paper is not yet published.

[2] C. T. Zahn, *loc. cit.*

10 milliamperes. The circuits were shielded from each other and run from independent batteries. The oscillation of A was maintained constant at 400 kilocycles generating waves of $\lambda = 750$ m. while that of B was adjusted by variable condensers $K_1$ and $K_2$. The high frequency oscillations fell on the aerial T and was amplified in another circuit C to obtain the beat tone in the loud speaker L. By adjusting $K_1$, $K_2$ this beat tone was maintained in unison with an electrically driven fork not shown in the figure. Thus the frequency of B could always be brought to a fixed value. The liquid in question was introduced in a condenser which was joined in parallel with $K_1$ and $K_2$. These were Radio-precision condensers of which $K_1$ read up to 3 m. mf. and $K_2$ a vernier condenser, read up to 0·4 m. mf. The importance of accurately calibrating these condensers has been pointed out by Zahn and others [1] in their measurements on gases. In the present case calibration was performed in the following manner. A and B were identical circuits, so that the beat tone in the loud speaker could be adjusted to unison with the fork either by varying the capacities of $K_1$ and $K_2$ in circuit B or by varying the capacities of the corresponding condensers in the circuit A.

To calibrate $K_1$, unison with the fork was initially obtained with a particular value of $K_1$; next an air condenser similar to $K_2$ was introduced in parallel with $K_1$ and $K_2$ and unison re-established by varying condensers in the circuit A. Now the air condenser was removed from the circuit and unison was established again by varying $K_1$ and $K_2$. It would not be out of place to mention here that $K_1$ should be calibrated independently of $K_2$ so that $K_2$ should be changed as slightly as possible. Thus by alternately introducing and removing the air condenser, $K_1$ was calibrated throughout the scale. The readings of $K_1$ were read from a big circular scale of 50 cm.

[1] loc.cit.
E. O. Fritts, Phys. Rev., 23, 345 (1924).

diameter with the help of a long glass pointer attached to the condenser. This magnified the scale sufficiently and provided an easy means of setting the condenser truly to some particular value. $K_2$ was calibrated in a similar manner, but this time instead of the air condenser the change of capacity required to obtain unison with the fork on both sides of the high frequency silence position was taken as the step and the unison was obtained by alternately changing $K_2$ and the corresponding condenser in the circuit A, all the other condensers remaining fixed. Next the values of the smallest divisions of $K_1$ and $K_2$ were compared at different positions of $K_1$ and the ratio of the two corrected scales found out. These capacities were shielded from external influences by earthed tin foils.

The method of operation in the case of dielectric constant measurement was to obtain the high frequency beat tone initially in unison with the fork and to re-establish unison when the measuring condenser was introduced. This was done by varying $K_1$ and $K_2$, the other circuit remaining unaltered. Since the frequency remained constant the change of capacity was only to compensate for placing the measuring condenser in parallel with $K_1$ and $K_2$; thus the difference of condenser-readings gave the capacity of the liquid condenser. It was observed that even when the batteries were in good condition the valves took some time to reach a steady state; the circuits were therefore initially run for about half an hour to obtain steady unison before measurements could be started.

The measuring condenser consisted of two concentric gold-plated brass cylinders A and B mounted in a glass bulb as shown in fig. 2. The inside cylinder was closed at both ends and a gold-plated brass rod attached to the upper end was fitted in the glass capillary and fused there by means of a platinum wire welded to the rod. The outer cylinder was open at both ends and held tightly by two rectangular
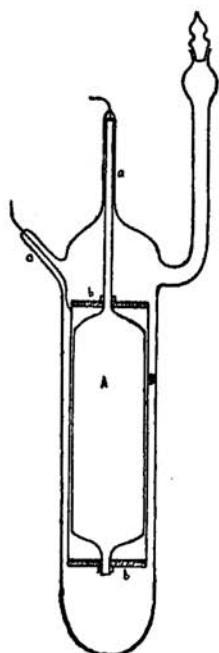
Fig. 2.

glass pieces 'b','b' with screws attached to the centre rod and a platinum wire welded to it was fused to the small side tube 'c'. The cylinders were fixed at 1 mm. apart and the air-capacity of the condenser was 42 m.m.f. This was found by perfectly drying the glass bulb and finding the capacity of the dry condenser. The capacity of the condenser was then found with the liquid inside it and the ratio of the two values gave the dielectric constant of the liquid. But the capacity of the measuring condenser consisted of two parts; one was the fixed capacity due to the leads and insulation which did not vary with the dielectric constant of the liquid and the other was the capacity between the cylinders which was directly proportional to the dielectric constant. To eliminate the first part an imitation lead was prepared and mounted in a similar glass bulb and its capacity was determined in the same position as in the experiment proper. Several readings gave consistent results and this correction was applied to all subsequent capacity measurements. The air-capacity of the measuring condenser was examined for temperature variation but no appreciable change was observed, and its value was checked from time to time. In the case of liquid measurements, the bulb was dried perfectly and the liquid was introduced to fill the capillary and the side-tube completely.

The glass bulb containing the measuring condenser was clamped by a wooden stand in a bath of distilled water for which a glass thermostat 10″ in diam. and 12″ high was employed. This was jacketed with asbestos sheet and cotton, and the temperature was maintained uniform by means of a glass stirrer and recorded by a mercury thermomenter reading

up to ·1°C. It was observed that the level of water in the bath had some influence on capacity measurements ; for this reason the same level was always maintained, and the correction mentioned above was found for the same position of the water level. All metal parts were avoided and the capacities were changed with long glass rods from a distance. Measurements were made at intervals of 10°C and the readings were noted when the beat tone remained steady for about ten minutes confirming temperature equilibrium within the liquid in question.

The density of the mixtures was determined by a special form of density bottle shown in fig. 3. This consisted of a glass bulb A of 30 cc. capacity with a stoppered overflow bulb B with good ground glass joint at 'a'. The bulb with B attached to it tightly was filled with the liquid in question with excess of liquid in the bulb B. This was then hung by a thread and immersed in the water bath and when the temperature equilibrium was established the level of the liquid was adjusted to a definite scratch 'b' by introdncing small capillary tubes in B. The stopper C was then fitted tightly and the vessel allowed to come to room temperature before weights were taken.
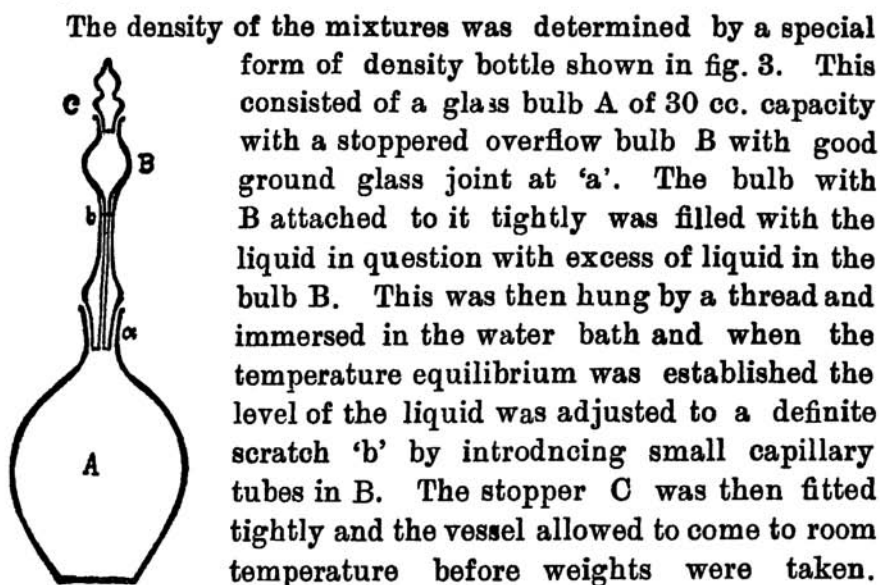
Fig. 3.    The density and capacity measurements were carried out simultaneously. The bottle was calibrated from standard density values for water and has been found very convenient for volatile liquids.

The materials used were Merck's carbon tetrachloride redistilled over calcium chloride and Kahlbaum's chlorobenzene and bromobenzene specially prepared for refractive index measurement. The density values were checked and found to agree with tabular results in Landolt "Tabellen". The liquids were accurately weighed in stoppered bottles and great care was exercised in making up the solution to avoid evapora-

tion in the process of mixing and transfering.  The same samples were used throughout the measurement.

### Data and Results.

Several solutions of chlorobenzene and bromobenzene in carbon tetrachloride were employed, of which about eight were low concentration solutions for each, and their dielectric constants and densities were  determined at temperatures ranging from 10° to 60°C.  The results were collected in tables I and II and the dielectric constants and densities were for comparison plotted against molecular concentration at 10° and 60°C (figs. 4 and 5).  P was  then  calculated and $P_2$ found out.
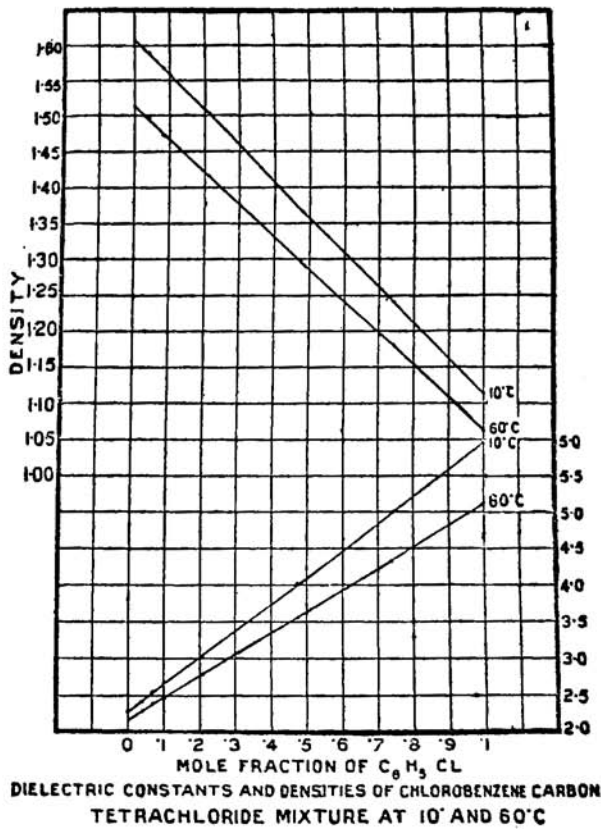
Fig. 4.



DIELECTRIC CONSTANTS AND DENSITIES OF CHLOROBENZENE CARBON
TETRACHLORIDE MIXTURE AT 10° AND 60°C

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Fig. 5.



DIELECTRIC CONSTANT AND DENSITIES OF BROMOBENZENE
CARBON TETRACHLORIDE MIXTURES AT 10° AND 60°C
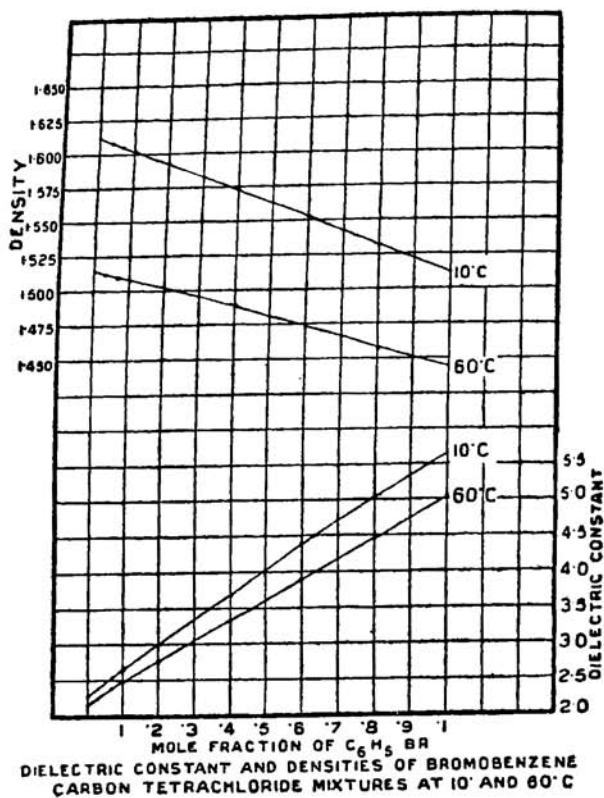
These results were collected in tables III and IV, and the values of P were plotted against concentration in figs. 6 and 7. Something should however be said regarding the calculation of $P_2$. Carbon tetrachloride has theoretically no moment, so that it should give a constant molecular polarisation; but as has been pointed out by Graffunder,[1] Grützmacher[2] and others in the case of benzene, the molecular polarisation of carbon tetrachloride increases slightly with temperature.

[1] W. Graffunder, Ann. d. Physik, 70, 232 (1923).

[2] M. Grützmacher, Zeitu. f. Physik, 28, 349 (1924).

Fig. 6.



POLARISATION (P) OF CHLOROBENZENE IN CARBONTETRA CHLORIDE SOLUTION AT DIFFERENT TEMPARATURES.

Fig. 7.



POLARISATION ($P_2$) OF BROMOBENZENE IN CARBON TETRACHLORIDE
SOLUTIONS AT DIFFERENT TEMPARATURES.
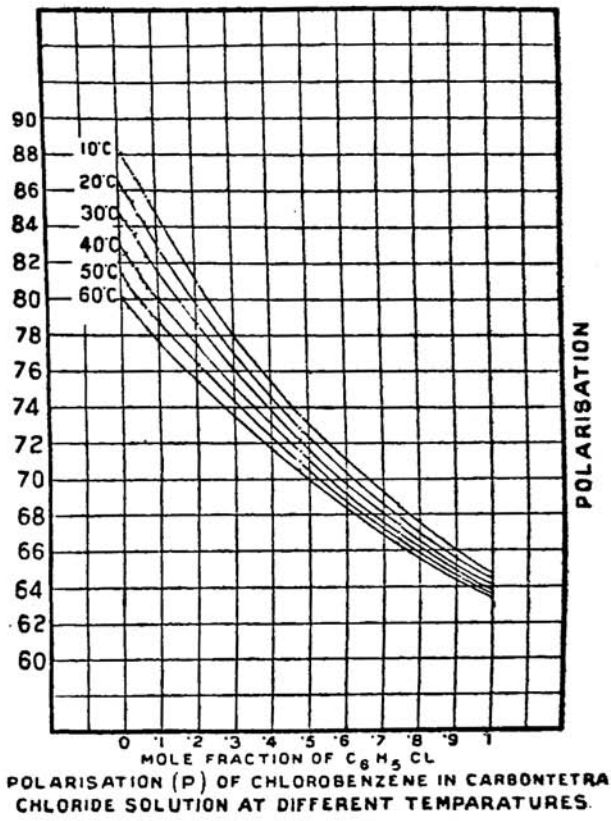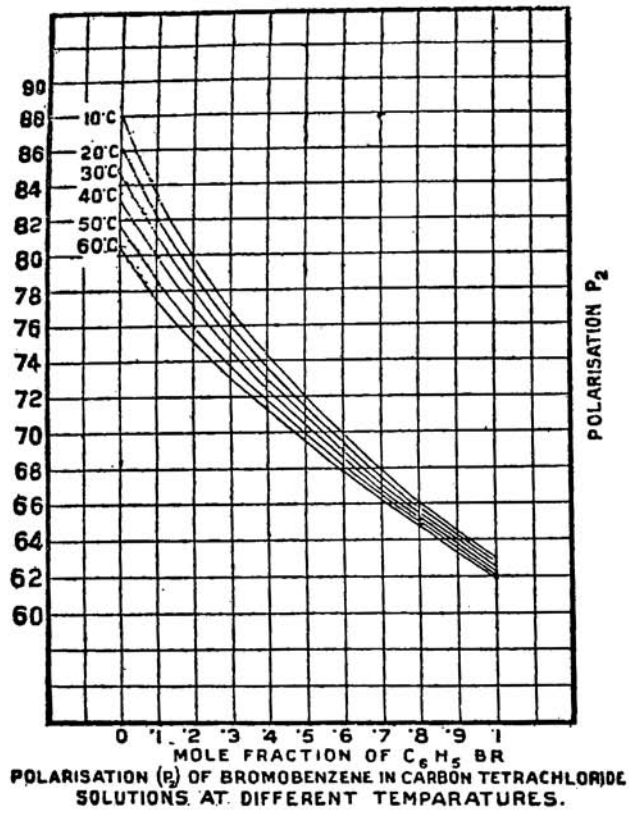
This would enormously affect the value of $P_2$ at low concentration; so to avoid unnecessary errors $P_2$ was calculated from the particular values of $P_1$ obtained at the corresponding temperatures and the same samples were always used. This procedure also avoids any effect of slight impurity present in the solvent. $P_2$ was then plotted against $O_2$ (figs. 8 and 9) and the curves were extrapolated to obtain the zero concentration intercepts. The low concentration points show a little diver-

Fig. 8.



MOLE FRACTION OF $C_6H_5CL$

POLARISATION (P) OF CHLOROBENZENE-CARBONTETRA CHLORIDE MIXTURES AT 10° AND 60° C

Fig 9.



POLARISATION (P) OF BROMOBENZENE-CARBON TETRACHLORIDE
MIXTURES AT 10° AND 60° C.
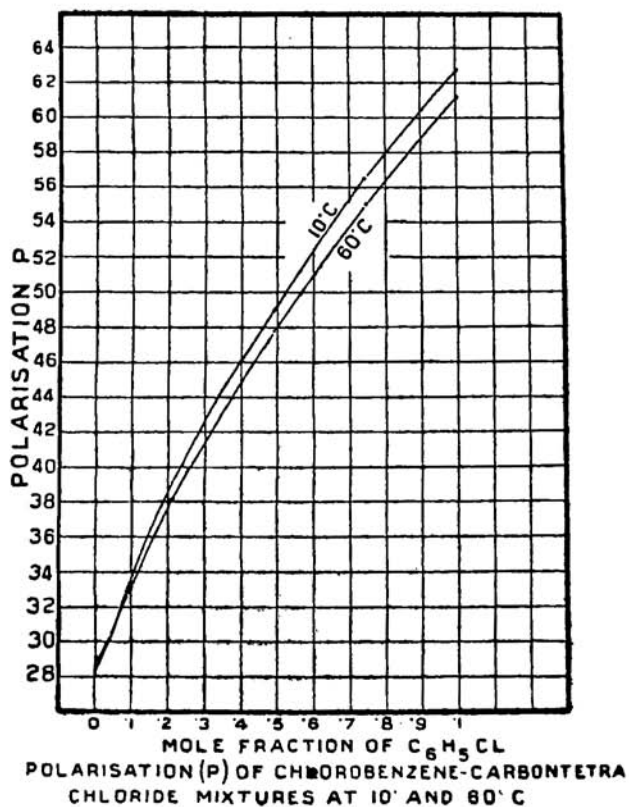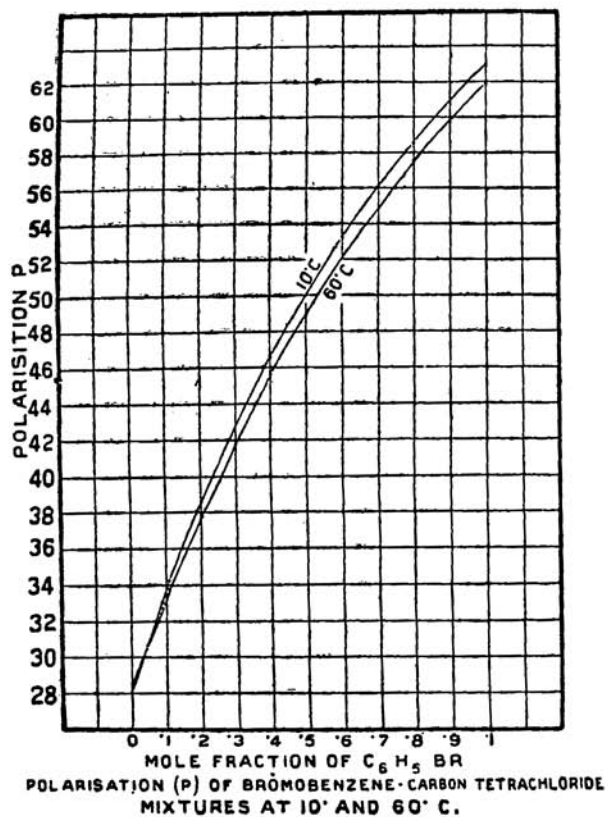
gence, but the average direction cannot be mistaken and the intercepts were well-defined. To test Debye theory the intercepts $P_a$ were plotted against $\frac{1}{T}$ (fig. 10).

Fig. 10.



VARIATION OF $P_\infty$ WITH $\frac{1}{T}$ FOR CHLOROBENZENE AND BROMOBENZENE
SOLUTIONS IN CARBON TETRACHLORIDE
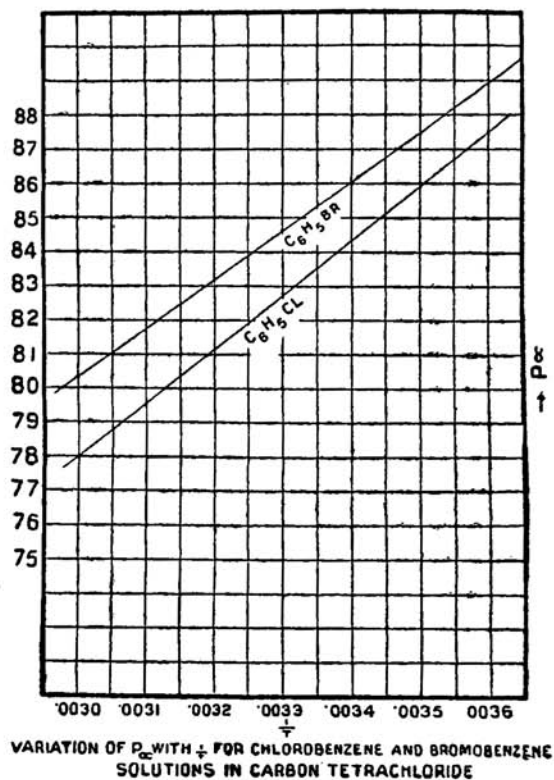
*Discussion of results.*

It would be observed from the curves with $P_2$ versus $C_2$ that the substances show the simplest type of association. The curves are quite regular and association increases with concentration and temperature as was expected from theory. Curves with $P_a$ and $\frac{1}{T}$ do not show any systematic curvature

even when drawn on a big graph paper but practically give straight lines standing strongly in favour of Debye theory. The moments and the optical data were then calculated from these curves. The values of A come out to be nearly equal to the molecular refraction term extrapolated to infinite wavelength and are shown in table V. Of course such a low range of temperature as adopted here does not admit of extrapolation to a very high temperature; but the practically constant values of B obtained theoretically from different values of $P_\alpha$ indicate that the moment would be very nearly the same. Most of the investigators in this line obtained the curves of $P_2$ *versus* $C_2$ with ordinary concentrations and extrapolated them to zero concentration but it has been observed that extrapolation from ordinary concentration is not at all reliable; besides they calculated the moment on the assumption of the validity of Debye equation $P = A + \frac{B}{T}$ holding at

zero concentration. But the method adopted here is quite independent and satisfactory. The values tabulated above agree with the values obtained by Hojendahl and Smyth and Morgan within limits of experimental error. As regards the experimental method it has been observed that P and $P_1C_1$ become so nearly equal at low concentration that their difference is not so reliable below ·03 conc. unless the dielectric data can be obtained up to four decimal figures, and an error of ·05% in the dielectric value there involves an error of 1% in the value of $P_2$. For this reason smooth curves were drawn with dielectric constants and densities plotted against concentration and the values for calculating P were taken from these curves. Small bubbles were observed to form in the condenser at high temperatures between 50° to 60° C, but the values of dielectric constants remained practically unaltered when all the measurements were repeated during cooling. As regards density measurements, low temperatures gave some trouble, for when the liquid expanded at room temperature air tried to escape through the side of the stopper C along with

some vapour. This difficulty was got over by tightly pressing the glass stopper occasionally and the error in any case did not exceed ·02%. Work with iodobenzene is in progress and then we shall be in a position to study in a generalised manner the nature of the curves of $P_2$ *versus* $C_2$ for these simple substituted compounds. In conclusion we express our heartfelt thanks to Prof. S. N. Bose for his kind guidance aud helpful interest throughout the work.

*Summary.*

Dielectric constants of solutions of chlorobenzene and bromobenzene in carbon tetrachloride have been accurately measured by the Heterodyne method and their densities determined by a special form of density bottle.

The molecular polarisation was calculated and curves were drawn with partial polarisation and concentration of the polar liquids. The zero concentration intercepts gave values which satisfy Debye formula $P = A + \frac{B}{T}$ The moments of these liquids were calculated. It was observed that association increases with concentration and temperature.

TABLE I.

Dielectric constants and densities of chlorobenzene carbon tetrachloride solutions at different temperatures, the upper value being the dielectric constant and the lower one the density.

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| Molar fraction of C₆H₅Cl | TEMPERATURES. | | | | | |
|---|---|---|---|---|---|---|
| | 0°C | 20°C | 30°C | 40°C | 50°C | 60°C |
| 0 | 2·260 | 2·241 | 2·223 | 2·205 | 2·186 | 2·167 |
| | 1·6180 | 1·5940 | 1·5748 | 1·5551 | 1·5356 | 1·5156 |
| ·009201 | 2·294 | 2·273 | 2·253 | 2·233 | 2·213 | 2·192 |
| | 1·6091 | 1·5899 | 1·5705 | 1·5506 | 1·5314 | 1·5108 |
| ·02113 | 2·337 | 2·314 | 2·292 | 2·271 | 2·247 | 2·226 |
| | 1·6027 | 1·5838 | 1·5644 | 1·5454 | 1·5255 | 1·5062 |
| ·03690 | 2·398 | 2·368 | 2·343 | 2·318 | 2·293 | 2·270 |
| | 1·5940 | 1·5755 | 1·5565 | 1·5371 | 1·5180 | 1·4984 |
| ·04258 | 2·414 | 2·388 | 2·362 | 2·336 | 2·310 | 2·285 |
| | 1·5915 | 1·5725 | 1·5536 | 1·5343 | 1·5151 | 1·4959 |
| ·05796 | 2·470 | 2·440 | 2·412 | 2·382 | 2·354 | 2·329 |
| | 1·5828 | 1·5644 | 1·5460 | 1·5264 | 1·5076 | 1·4886 |
| ·07562 | 2·535 | 2·503 | 2·469 | 2·437 | 2·407 | 2·378 |
| | 1·5745 | 1·5560 | 1·5374 | 1·5184 | 1·4992 | 1·4806 |
| ·08465 | 2·567 | 2·533 | 2·498 | 2·464 | 2·432 | 2·403 |
| | 1·5685 | 1·5508 | 1·5325 | 1·5133 | 1·4946 | 1·4758 |
| ·1055 | 2·641 | 2 604 | 2·568 | 2·532 | 2·498 | 2·463 |
| | 1·5580 | 1·5409 | 1·5227 | 1·5042 | 1·4855 | 1·4667 |
| ·2149 | 3·040 | 2·982 | 2·928 | 2·876 | 2·824 | 2·774 |
| | 1·5031 | 1·4859 | 1·4686 | 1·4513 | 1·4338 | 1·4162 |
| ·4810 | 4·021 | 3·919 | 3·821 | 3·732 | 3·650 | 3·575 |
| | 1·3696 | 1·3548 | 1·3400 | 1·3246 | 1·3100 | 1·2949 |
| ·7427 | 5·008 | 4·864 | 4·728 | 4·594 | 4·478 | 4·363 |
| | 1·2445 | 1·2319 | 1·2188 | 1·2057 | 1·1932 | 1·1808 |
| 1 | 5·956 | 5·778 | 5·602 | 5·437 | 5·290 | 5·154 |
| | 1·1170 | 1·1065 | 1·0955 | 1·0849 | 11·074 | 1·0684 |

TABLE II.

Dielectric constants and densities of bromobenzene-carbontetrachloride solutions at different temperatures, the upper value being the dielectric constant and the lower one density.

| Molar fraction of $C_6H_5Br$. | Temperatures. | | | | | |
|---|---|---|---|---|---|---|
| | 10°C | 20°C | 30°C | 40°C | 50°C | 60°C |
| 0 | 2·260 | 2·241 | 2·223 | 2·205 | 2·186 | 2·167 |
| | 1·6130 | 1·5940 | 1·5748 | 1·5551 | 1·5356 | 1·5156 |
| ·010014 | 2·297 | 2·276 | 2·256 | 2·237 | 2·216 | 2·19 |
| | 1·6122 | 1·5932 | 1·5788 | 1·5543 | 1·5347 | 1·5151 |
| ·02049 | 2·335 | 2·312 | 2·291 | 2·269 | 2·247 | 2·225 |
| | 1·6112 | 1·5920 | 1·5780 | 1·5535 | 1·5340 | 1·5138 |
| ·04110 | 2·410 | 2·384 | 2·359 | 2·335 | 2·310 | 2·285 |
| | 1·6100 | 1·5905 | 1·5710 | 1·5518 | 1·5328 | 1·5130 |
| ·04898 | 2·438 | 2·411 | 2·385 | 2·359 | 2·333 | 2·360 |
| | 1·6090 | 1·5900 | 1·5705 | 1·5512 | 1·5320 | 1·5124 |
| ·06420 | 2·493 | 2·464 | 2·436 | 2·408 | 2·379 | 2·352 |
| | 1·6075 | 1·5888 | 1·5692 | 1·5500 | 1·5310 | 1·5116 |
| ·07837 | 2·545 | 2·514 | 2·484 | 2·453 | 2·422 | 2·393 |
| | 1·6058 | 1·5877 | 1·5680 | 1·5488 | 1·5302 | 1·5108 |
| ·08770 | 2·576 | 2·544 | 2·513 | 2·481 | 2·450 | 2·418 |
| | 1·6045 | 1·5866 | 1·5672 | 1·5480 | 1·5298 | 1·5103 |
| ·1098 | 2·658 | 2·622 | 2·587 | 2·553 | 2·518 | 2·483 |
| | 1·6025 | 1·5848 | 1·5660 | 1·5464 | 1·5295 | 1·5090 |
| ·2020 | 2·989 | 2·942 | 2·893 | 2·843 | 2·792 | 2·744 |
| | 1·5931 | 1·5760 | 1·5576 | 1·5395 | 1·5215 | 1·5083 |
| ·4000 | 3·697 | 3·613 | 3·538 | 3·467 | 3·400 | 3·337 |
| | 1·5731 | 1·5564 | 1·5397 | 1·5224 | 1·5060 | 1·4892 |
| ·6000 | 4·400 | 4·288 | 4·182 | 4·090 | 4·003 | 3·917 |
| | 1·5521 | 1·5366 | 1·5211 | 1·5053 | 1·4898 | 1·4743 |
| ·8000 | 5·030 | 4·900 | 4·782 | 4·677 | 4·580 | 4·488 |
| | 1·5315 | 1·5166 | 1·5032 | 1·4875 | 1·4730 | 1·4586 |
| 1 | 5·642 | 5·490 | 5·349 | 5·212 | 5·090 | 4·975 |
| | 1·5122 | 1·4988 | 1·4850 | 1·4715 | 1·4578 | 1·4446 |

## TABLE III.

Polarisations of chlorobenzene-carbontetrachloride solutions at different temperatures, the upper value being the polarisation (P) of the solution and the lower one the polarisation ($P_2$) of the solute.

| Molar fraction of $C_6H_5Cl$ | Temperatures. | | | | | |
|---|---|---|---|---|---|---|
| | 10°C | 20°C | 30°C | 40°C | 50°C | 60°C |
| $C_2=0$ <br> M=153.84 | 28·210 | 28·241 | 28·291 | 28·348 | 28·384 | 28·427 |
| $C_2=·009201$ <br> M=153.46 | 28·742 <br> 86·04 | 28·756 <br> 84·22 | 28·789 <br> 82·12 | 288·27 <br> 80·42 | 28·853 <br> 79·36 | 28·884 <br> 78·10 |
| $C_2=·02113$ <br> M=152·97 | 29·424 <br> 85·66 | 20·419 <br> 83·99 | 29·435 <br> 82·43 | 29·456 <br> 80·78 | 29·450 <br> 78·83 | 29·465 <br> 77·55 |
| $C_2=·03690$ <br> M=152·32 | 30·301 <br> 84·88 | 30·278 <br> 83·47 | 30·265 <br> 81·78 | 30·247 <br> 79·81 | 30·223 <br> 78·22 | 30·233 <br> 77·38 |
| $C_4=·04258$ <br> M=152·08 | 30·610 <br> 84·57 | 30·592 <br> 83·45 | 30·565 <br> 81·70 | 30·541 <br> 79·85 | 30·510 <br> 78·31 | 30·490 <br> 67·88 |
| $C_2=·05796$ <br> M=151·44 | 31·464 <br> 84·35 | 31·397 <br> 82·69 | 31·348 <br> 81·03 | 31·291 <br> 79·12 | 31·238 <br> 77·62 | 31·231 <br> 76·81 |
| $C_2=·07562$ <br> M=150·72 | 32·401 <br> 83·63 | 32·331 <br> 82·33 | 32·225 <br> 80·31 | 32·148 <br> 78·60 | 32·097 <br> 77·48 | 32·041 <br> 76·22 |
| $C_2=·08465$ <br> M=150·34 | 32·888 <br> 83·47 | 32·784 <br> 81·91 | 32·671 <br> 80·03 | 32·581 <br> 78·35 | 32·500 <br> 77·01 | 32·460 <br> 76·07 |
| $C_2=·1055$ <br> M=149·48 | 33·924 <br> 82·38 | 33·796 <br> 80·90 | 33·697 <br> 79·53 | 33·592 <br> 78·05 | 33·512 <br> 76·99 | 33·408 <br> 75·64 |
| $C_2=·2140$ <br> M=145·00 | 39·046 <br> 78·85 | 38·822 <br> 77·69 | 38·690 <br> 76·60 | 38·440 <br> 75·51 | 38·238 <br> 74·43 | 38·047 <br> 73·38 |
| $C_2=·4310$ <br> M=133·97 | 49·08 <br> 71·60 | 48·77 <br> 70·91 | 48·45 <br> 70·21 | 48·22 <br> 69·65 | 47·97 <br> 69·10 | 47·79 <br> 68·68 |
| $C_2=·7427$ <br> M=123·16 | 56·57 <br> 66·89 | 56·28 <br> 65·99 | 55·99 <br> 65·59 | 55·68 <br> 65·14 | 55·42 <br> 64·78 | 55·15 <br> 64·41 |
| $C_2=1$ <br> M=112·58 | 62·76 | 62·47 | 62·18 | 61·88 | 61·65 | 61·45 |

## TABLE IV.

Polarisations of bromobenzene carbontetrachloride solutions at different temperatures, the upper value polarisation (P) of the solution and the lower one the polarisation ($P_2$) of the solute.

| Molar fraction of $C_6H_5Br$ | Temperatures | | | | | |
|---|---|---|---|---|---|---|
| | 10°C | 20°C | 30°C | 40°C | 50°C | 60°C |
| $C_2 = o$<br>$M = 153.84$ | 28.210 | 28.241 | 28.291 | 28.348 | 28.384 | 28.427 |
| $C_2 = .010014$ | 28.807 | 28.820 | 28.858 | 28.901 | 28.917 | 28.947 |
| $M = 153.87$ | 87.83 | 86.06 | 84.41 | 83.57 | 81.60 | 80.35 |
| $C_2 = .02049$ | 29.417 | 29.414 | 29.436 | 29.448 | 29.459 | 29.477 |
| $M = 153.90$ | 87.09 | 85.49 | 84.17 | 82.03 | 80.84 | 79.67 |
| $C_2 = .04110$ | 30.577 | 30.562 | 30.556 | 30.557 | 30.534 | 30.518 |
| $M = 153.97$ | 85.80 | 84.71 | 83.40 | 82.10 | 80.69 | 79.31 |
| $C_2 = .04893$ | 31.010 | 30.980 | 30.969 | 30.949 | 30.922 | 30.914 |
| $M = 153.99$ | 85.44 | 84.22 | 83.02 | 81.50 | 80.27 | 79.26 |
| $C_2 = .06420$ | 31.842 | 31.797 | 31.777 | 31.744 | 31.684 | 31.658 |
| $M = 154.04$ | 84.78 | 83.63 | 82.59 | 81.24 | 79.78 | 78.76 |
| $C_2 = .07837$ | 32.618 | 32.550 | 32.523 | 32.432 | 32.381 | 32.340 |
| $M = 154.08$ | 84.46 | 83.22 | 82.29 | 80.84 | 79.33 | 78.36 |
| $C_2 = .08770$ | 33.082 | 33.006 | 32.968 | 32.921 | 32.826 | 32.754 |
| $M = 154.12$ | 83.76 | 82.57 | 81.62 | 80.33 | 79.03 | 77.74 |
| $C_2 = .1098$ | 34.246 | 34.142 | 34.064 | 34.006 | 33.868 | 33.801 |
| $M = 154.18$ | 83.18 | 81.98 | 80.87 | 79.88 | 78.32 | 77.38 |
| $C_2 = .2020$ | 38.658 | 38.516 | 38.370 | 38.198 | 37.967 | 37.780 |
| $M = 154.48$ | 79.93 | 79.10 | 78.19 | 77.11 | 75.82 | 74.73 |
| $C_2 = .4000$ | 46.69 | 46.39 | 46.17 | 45.97 | 45.77 | 45.60 |
| $M = 155.10$ | 74.41 | 73.61 | 72.98 | 72.40 | 71.85 | 71.36 |
| $C_2 = .6000$ | 53.30 | 52.99 | 52.70 | 52.50 | 52.29 | 52.07 |
| $M = 155.73$ | 70.03 | 69.50 | 68.97 | 68.60 | 68.23 | 67.84 |
| $C_2 = .8000$ | 58.52 | 58.27 | 58.07 | 57.88 | 57.76 | 57.60 |
| $M = 156.36$ | 66.10 | 65.78 | 65.51 | 65.26 | 65.10 | 64.89 |
| $C_2 = 1$<br>$M = 156.99$ | 63.07 | 62.79 | 62.57 | 62.31 | 62.12 | 61.92 |

TABLE V.

| Substance | Pα | A | A calculated from optical data | B | λ |
|---|---|---|---|---|---|
| C₆H₅ Cl | ...86·4   at   10·C<br>84·5   ,.   20·<br>82·8   .,   30·<br>81·0   ,,   40·<br>79·5   ,.   50·<br>78·0   ,,   60· | 31·2 | 30·3 | 15600 | 1·59 × 10⁻¹⁸ |
| C₆H₅ Br | 88·0   at   10·C<br>86·2   ,,   20·<br>84·7   .,   30·<br>83·Ῑ   ,,   40·<br>81·7   ,.   50·<br>80·4   ,,   60· | 36·8 | 33·4 | 14500 | 1·53 × 10⁻¹⁸ |

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