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The Diamagnetism of Liquid Mixtures

By

Dr. S. Ramachandra Rao and G. Sivaramakrishnan,
Annamalai University.

Abstract.

The diamagnetic susceptibility values of binary liquid mixtures have been experimentally determined for the following eight cases—benzene and carbon disulphide, benzene and nitrobenzene, benzene and carbon tetrachloride, benzene and hexane, benzene and chlorobenzene, hexane and chlorobenzene, hexane and nitrobenzene and acetone and chloroform. Graphs drawn between the percentage composition by weight and the specific diamagnetic susceptibilities, give straight lines in all the above cases, showing that the additive law is obeyed to within half per cent., this being the maximum percentage error in our experiments. The significance of these results is discussed in the light of X-ray scattering by liquid mixtures.

1. *Introduction.*

The subject of diamagnetism in relation to molecular structure has been fully emphasised in a lecture by Sir C. V. Raman [1] before the Physical Society, London. Prof. Bhatnagar [2] has also shown the importance of a study of the

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[1] Sir C. V. Raman : Proc. Phy. Soc., **42**, 309 (1930).

[2] S. S. Bhatnagar and collaborators : Phil. Mag., **5**, 536 (1928); **6**, 217 (1928); **10** 101 (1930).

diamagnetic properties of liquids in elucidating the complex structure of molecules, especially in the case of isomers. It was therefore believed that it would be interesting to examine the diamagnetic susceptibilities of binary liquid mixtures in the light of the additive law.

When we were finally checking our measurements, a discussion was started in the pages of Nature by Ranganadham,[3] who questioned the accuracy of the results of Trew and Spencer.[4] These investigators found that in the case of acetone-chloroform and acetone-bromoform mixtures, there were serious departures from the additive law. For certain compositions, the mixtures were found to be even paramagnetic, this value attaining a maximum at some definite composition for each mixture. These results were obtained by using a Curie-Chenaveau balance at low magnetic fields. Ranganadham's measurements were made by the Quincke method, the surface of the liquid column in the capillary tube being photographed with and without the magnetic field. He found for the acetone-chloroform mixtures only about 2 to 3 per cent. variations from the additive law. This observation was supported by Buchner.[5] Prof. Aubel[6] has drawn attention to previous work in this direction by Smith and Smith[7] and Trifonov.[8] These authors showed that mixtures of some typical liquids did rot show any variations from the additive law. Our results vere obtained when we had no knowledge of their work and it has been found by us also that all our typical mixtures obey the additive law.

[3] S. P. Ranganadham : Nature, **127**, 975 (1931).

[4] Trew and Spencer : Proc. Roy. Soc., A, **131**, 209 (1931).
              Also Nature, **128**, 152 (1931).

[5] H. Buchner, Nature, **128**, 302 (1931).

[6] Aubel, Nature, **128**, 455 (1931).

[7] Reference given in Prof. Aubel's note (Ref. 6).

[8] Reference given in Prof. Aubel's note (Ref. 6).

2. *Experimental method.*

Ranganadham and Buchner have adopted the Quincke method and observed the depression of the surface of a liquid column in a capillary tube. We have adopted the Curie method.

The liquids were taken from freshly opened bottles, being of the purest quality from Kahlbaum's or Merck's. They were carefully distilled several times, the necessary precautions being taken. The physical constants like the density and the boiling point were determined for each liquid and the values obtained were found to agree closely with the standard determinations.

The susceptibilities of the mixtures were determined in the following manner. Two liquids, after purification, were mixed in different proportions by volume in a number of test-tubes using a one c. c. pipette. These test-tubes were laid aside for a few hours so that the mixtures might attain a common steady temperature. From a knowledge of the density of each of the two pure liquids, the percentage composition by weight of each mixture was calculated. In later experiments we have directly mixed known weights of the two liquids in weighing bottles and thus prepared several mixtures with different compositions.

Thin bulbs of soft glass just over one centimetre diameter were blown and fitted with tight-fitting ground stoppers. The deflection of the Curie balance was noted for each of these bulbs and was found to be just a few millimetres. The susceptibility of the mixture was determined by filling one of the bulbs and noting the deflection. If the same bulb is used successively with mixtures of different concentrations, the susceptibilities can be calculated in each case.

With the help of the torsion head, the position of the bulb was carefully arranged to give the maximum deflection.

By suitable paper discs, the bulb was arranged to lie in the line of symmetry of the inclined pole-faces. The reading of the spot of light was always adjusted to have nearly the same value with the magnetic field on. In this manner, great care was taken to bring the bulb in the same position every time fresh readings were taken. On removing the magnetic field, the spot of light was deflected and the reading was again observed. The average of a number of readings gave the correct value of the deflection in any case.

One difficulty was the viscosity of the torsion fibre. Our deflections were about 20 to 30 cms. A slow creeping of the zero, about 2 mm. per minute, was sometimes noted. To minimise these errors as much as possible, readings were taken after a definite interval of time with the field on or off. More consistent readings were thus obtained.

The Curie balance and the pole-pieces were enclosed in wooden boxes with glass fronts to prevent air-currents. A thermometer inserted in the chamber with its bulb near the bulb containing the liquid showed that the temperature in the chamber never rose by more than 3 degrees. In fact in all our measurements, the temperatures of the liquids were between 32 and 33°C.

The magnet used was a large one of the Pye's type capable of carrying 16 amperes. Our working current was only 4 amperes and hence the heating effect was very small. The currents were measured with an ammeter of the Cambridge Scientific Instruments Company, reading by estimation to 0.005 of an ampere.

The experimental bulbs were filled with the mixtures up to a definite mark on the neck. Hence the weights of the liquids enabled us to calculate the densities since in all cases the same volumes were taken. We do not believe that the density measurements in these cases are precise but we are sure that our density curves give correctly the variations of density values with composition.

Water has been chosen as our standard, its susceptibility being taken as 0·72 [9] at 32° C.

We have considered all possible errors and find that the maximum error in our values could not be more than half per cent.

3. Results.

In choosing our typical liquid mixtures, we have kept in view two points, one being the symmetry or asymmetry of shape and the other the polarity or non-polarity of the concerned molecules.

(a) Benzene and carbon disulphide.

Both these molecules are nonpolar.[10] But they differ from each other in shape though they are symmetric. It is well known that the benzene molecule is flat and disc-shaped, the diameter and thickness being 6·2 and 3·2 A.U.[11] These values represent the effective closeness of approach of neighbouring molecules to any given molecule on its edge and side respectively. The carbon disulphide molecule on the other hand may be considered to be an elongated molecule, 5·75 A.U. being the length and 2·84 A.U. the diameter of the cross-section of the molecule.[12] We have therefore in these mixtures two types of molecules both being non-polar and symmetric but having different shapes.

The values of the specific diamagnetic susceptibilities (χ) are given in the following table. (Table I.)

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[9] In this paper, all susceptibility values should be multiplied by —10⁻⁶.

[10] Debye, Polar Molecules, pp. 50, 51 (1929).

[11] Sogani, Ind. Jour. Phys., 2, 97 (1927).

[12] I. R. Rao, Ind. Jour. Phys., 2, 451 (1928).

TABLE I.

Benzene and carbon disulphide.

Percentage of benzene by weight in the mixture.	Density.	χ.
0·0	1·265	0·550
6·2	1·230	0·557
10·3	1·205	0·566
16·6	1·175	0·575
21·3	1·133	0·581
25·3	...	0·589
30·3	1·109	0·594
40·5	...	0·610
50·3	1·031	0·625
62·9	0·980	0·645
69·3	0·967	0·655
75·5	0·946	0·664
79·8	0·933	0·672
85·4	0·917	0·678
88·9	0·908	0·684
94·1	0·896	0·690
100·0	0·878	0·702

Ishiwara[13] has given for benzene the value 0·712 as the specific diamagnetic susceptibility at 16·2° C.   Trew and Spencer obtained 0·732 for this liquid.   Our value, 0·702 at 32°C is in agreement with those given above, especially with that of Ishiwara.

[13] Landolt-Bornstein Tabellen : p. 1204 (1923).

(b)   Benzene and nitrobenzene.

The benzene molecule is symmetric and non-polar while the nitrobenzene molecule is highly asymmetric and intensely polar. There is also considerable evidence to show that at ordinary temperatures, there is a high degree of molecular association in nitrobenzene.[14]   The results are given below.

TABLE II.

Benzene and nitrobenzene.

Percentage of benzene by weight in the mixture.	Density.	χ.
0	1·200	0·513
11·1	1·153	0·537
18·3	—	0·544
29·8	1·081	0·572
41·7	1·040	0·596
49·2	1·015	—
59·5	10·983	0·629
70·7	—	0·642
77·3	0·932	0·679
89·9	0·897	0·689
100·0	0·872	0·702

(c)   Benzene and carbon tetrachloride.

The two types of molecules in this mixture are both symmetric and nonpolar but are different in shape. While the benzene molecule is flat and disc-shaped, the tetrachloride molecule is almost spherical, having a diameter of 5·3 A.U.[15]

[14]   S. R. Rao, Ind. Jour. Phys., 3, 1 (1928).
[15]   Sogani, Ind. Jour. Phys., 2, 377 (1928).

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TABLE III.

Benzene and carbon tetrachloride.

Percentage of benzene by weight in the mixture.	Density.	χ.
0·0	1·592	0·432
10·5	1·467	0·459
21·3	—	0·489
36·0	1·229	0·530
49·9	1·132	0·566
61·5	1·059	0·596
70·9	1·008	0·622
80·0	0·965	0·643
88·6	0·926	0·666
100·0	0·878	0·701

This mixture has also been worked by Trew and Spencer. Their value for pure carbon tetrachloride is 0·542 which is much higher than ours. Pascal[16] however has recorded a value of 0·429 at 15°C which is almost equal to our measurement.

(d) Benzene and hexane.

As in the last case, we have here two types of molecules, both non-polar and symmetric but having different shapes. The hexane molecules are long molecules, having a length of 9·8 A.U. and a cross-sectional diameter of 4·9 A.U.[17] The results are given below in Table IV.

Our value of the density of hexane is 0·683 at 30°C while the most reliable data is that of Young[18] who has given the value of 0·6505 at the same temperature. Our value appears

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[16] Pascal, values taken from references in Trew and Spencer's paper.

[17] G. W. Stewart, Phys. Rev., 31, 177 (1928); Sogani, *loc. cit.*

[18] L. B. Tabellen, p. 276 (1923).

to be much less than what one would expect to get even after allowing a good margin of error. We took the greatest care to purify the sample and the liquid used was collected after repeated distillations. It may be that there was some impurity—a longer chain compound of the paraffin series in the liquid. But the fact that this impurity has not in any manner modified the results gives more conclusive evidence of the additive nature of the susceptibility of liquid mixtures. The higher value of the density was noted by us at the end of our work and from the interest arising therefrom, we have decided to report the actual results.

TABLE IV.

Benzene and hexane.

Percentage of benzene by weight in the mixture.	Density.	χ.
0·0	0·683	0·839
6·3	0·694	0·835
11·8	0·700	0·825
15·3	0·705	0·814
22·0	0·717	0·808
27·3	0·726	0·797
39·1	0·747	0·782
48·1	0·762	...
60·6	0·786	0·754
73·7	0·814	0·735
80·3	0·828	0·723
87·4	0·845	...
88·4	0·849	0·716
95·2	0·862	0·711
100·0	0·878	0·700

(e) *Benzene and chlorobenzene.*

This case is similar to the case of benzene and nitro-benzene. The chlorobenzene molecule is however less polar than nitrobenzene. The values are given below.

TABLE V.

Benzene and chlorobenzene.

Percentage of benzene by weight in the mixture.	Density.	χ.
0·0	1·105	0·618
5.8	1·088	0·622
11·0	1·073	0·624
15·7	1·060	0·631
21·7	...	0·635
26·4	1·031	0·639
32·3	1·017	...
41·7	0·994	...
51·0	0·973	0·660
61·3	0·950	0·669
70·1	0·93z	0·673
75·0	0·923	0·678
80·3	0·912	6·682
85·3	0·903	0·687
89·7	0·896	0·690
94·9	0·884	0·696
100·0	0·878	0·700

(f) *Hexane and chlorobenzene.*

This case is similar to the previous case with this difference that the types of molecules have nothing in common between them. The molecule of benzene however is similar

to the chlorobenzene molecule except for the extra weight of the chlorine atom at some point on the rim. The results are tabulated below.

TABLE VI.

Hexane and chlorobenzene.

Percentage by weight of hexane in the mixture.	Density.	χ.
0·0	1·111	0·622
10·9	1·044	0·636
20·3	0·990	0·664
27·9	0·936	0·695
40·9	0·893	0·709
50·9	0·849	0·733
60·8	0·810	0·751
70·8	0·775	0·771
80·6	0·742	0·795
89·2	0·717	0·814
100·0	0·683	0·840

(g) *Hexane and nitrobenzene.*

This case is similar to the previous case. The results are given below.

TABLE VII.

Hexane and nitrovenzene.

Percentage by weight of hexane in the mixture.	Density.	χ.
0·0	0·510	1·202
8·2	0·531	...
21·9	0·579	1·042
29·9	0·604	0·994
40·5	0·640	0·930
51·6	0·678	0·872
61·3	0·712	0·825
71·4	0·743	0·782
80·6	0·776	0·748
90·5	0·811	0·715
100·0	0·840	0·683

(h) Acetone and chloroform.

Both these types of molecules are asymmetric in shape and polar. This mixture is also interesting because of the fact that Trew and Spencer have reported that between certain concentrations, the susceptibility attains positive values.

When these mixtures were prepared, there was a large amount of heat developed showing that there was some reaction going on in the mixture. The mixtures were however cooled down to the atmospheric temperature before the measurements were made. It is difficult therefore to explain this extraordinary behaviour unless it be that the compounds formed, if any, have just the total susceptibility of the constituents. The results are tabulated below.

TABLE VIII.

Acetone and chloroform.

Percentage by weight of acetone in the mixture.	Density.	χ.
0·0	1·476	0·494
12·0	1·338	0·506
21·1	1·248	0·511
29·8	1·174	0·523
40·8	1· 90	0·531
50·2	1·030	0·542
61·2	0·969	0·555
70·0	0·923	·0·569
78·7	0·881	0·574
88·1	0·840	0·585
100·0	0·794	0·595

It is interesting to compare these values with those of other investigators. Our values for pure acetone and chloroform are 0·595 and 0·494.

For the latter liquid, Meslin [19] has recorded 0·58 as the diamagnetic susceptibility at 20°C. Pascal's [20] measurements gave values of 0·581 and 0·488 for the two liquids. Trew and Spencer have obtained 1·229 and 0·596 for acetone and chloroform respectively. Buchner [21] gives 0·58 and 0·485 for the two liquids. Our values agree remarkably well with the measurements of Buchner and Pascal. The values of Trew and Spencer seem to be much higher than the actual values.

As will be evident from Table VIII, there is a gradual change in the value of the susceptibility of the mixture as the concentration of one is increased. But there is no evidence of any paramagnetic value at intermediate concentrations.

(i) Composition-susceptibility curves.

Trew and Spencer have drawn graphs between the composition in moles per cent. of one of the two liquids in the mixture and the specific diamagnetic susceptibility. We believe that such graphs do not have any significance. Pascal's additive law for molecules states that the molecular susceptibility for one type of molecules is equal to the sum of the atomic susceptibilities of the constituent atoms and a factor depending on the structure of the molecule. Each molecule is exactly like another and when we get to molecular dimensions there is perfect homogeneity. But in a mixture of two liquids this does not happen to be the case. This point will be dealt with at some length later. We believe that it would be more proper to apply the law used for solutions. If in unit mass of the mixture, we have m grammes of one of the two liquids, χ_1 and χ_2 are the susceptibilities of the liquids, then the susceptibility of the mixture $\chi = (1-m)\chi_1 + m\chi_2$; or $\chi = \chi_1 + m(\chi_2 - \chi_1)$. This may be taken as the additive law for mixtures.

[19] Meslin, Landolt Bornstein Tabellen, p. 1204 (1923).

[20] Pascal, values taken from references in Trew and Spencer's papers.

[21] H. Buchner, loc. cit.

We have therefore drawn graphs (see Figs. 1, 2 and 3) between the composition by weight of one of the two liquids in the mixture and the susceptibility.

If it is only a mechanical mixture, one would not expect any deviation from the above simple law. There will be deviations only if there are any chemical reactions between the liquids. All the curves drawn in figures 1, 2 and 3 are found to be straight lines.
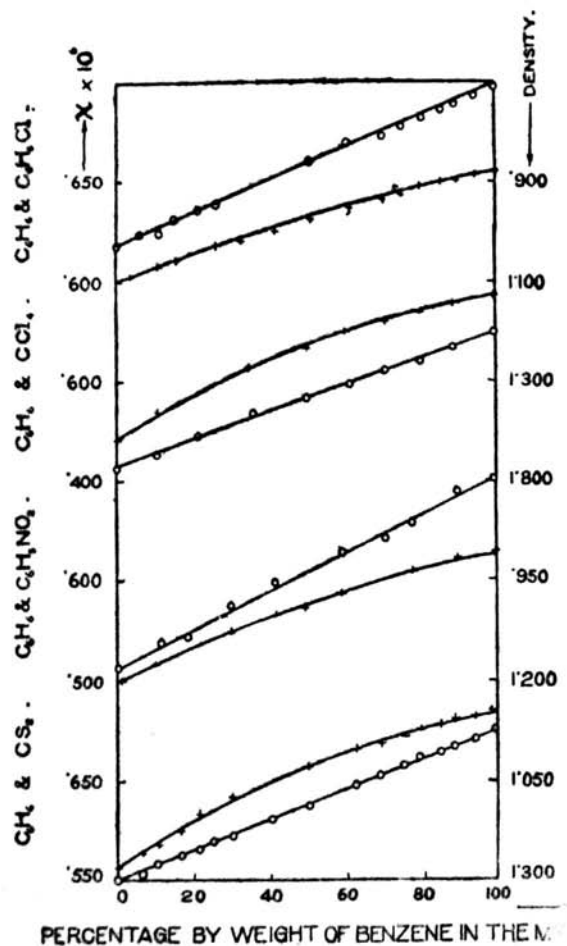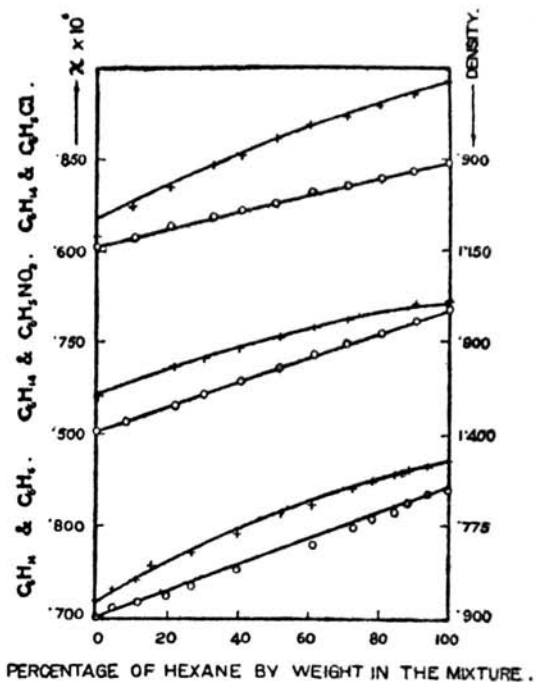
FIG. 1.

PERCENTAGE OF HEXANE BY WEIGHT IN THE MIXTURE.

FIG. 2.

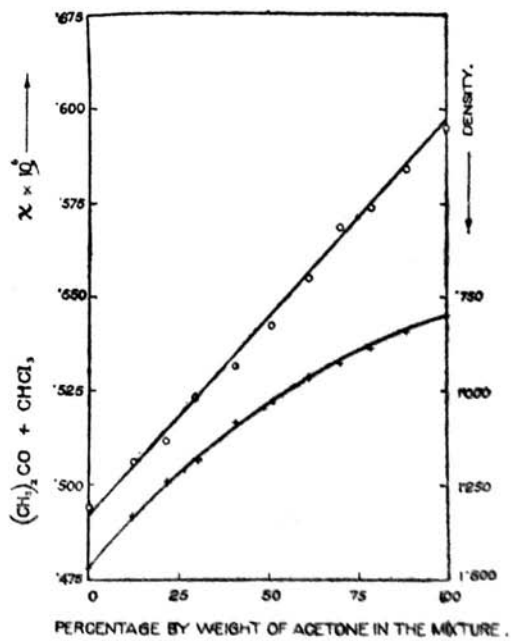PERCENTAGE BY WEIGHT OF ACETONE IN THE MIXTURE.

FIG. 3.

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(j) Composition-density curves.

For the sake of comparison, we have also drawn in the above figures curves between composition and density at 30°C. It will be noticed that the variations are between 2 and 5 per cent. In passing, we want to mention that the density variations are more striking when we are working with mixtures of entirely different shapes like acetone and chloroform or benzene and carbon tetra-chloride.

4. *The probable anomaly at low concentrations.*

We desire to draw attention to an anomaly we have noticed at low concentrations (less than about 10 per cent.). The specific susceptibility of the mixtures at these concentrations did not fall on the straight line curves in all cases. Though these mixtures were repeated several times, there were always consistently small departures from the additive law. But these variations were always less than half per cent., which makes it difficult for us to assert this point definitely. But judging from our observations, the consistency of the values obtained and the mean about which the values in any particular case distribute themselves, there seems to be considerable evidence to show that at low concentrations, we have small departures from the additive law. There are many interesting theoretical possibilities arising from this observation but it is too early to discuss the matter at this stage. We are now engaged in improving the technique to get higher sensitivity and shall then make a report on this interesting possibility.

5. *Discussion.*

The study of X-ray diffraction in liquids[22] has gradually fixed our ideas regarding the structure of liquids.

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[22] See numerous papers in the Ind. Jour. of Physics by Sir C. V. Raman's students and in the Phys. Rev. by Stewart and his students.

Krishnamurti[23] and more recently Meyer[24] have studied the diffraction patterns produced by liquid mixtures. Their results indicate that a new peak is obtained in the case of mixtures of perfectly miscible liquids. This shows that a new spacing has been formed within the mixture. If the liquids are not perfectly miscible, the original spacings are still present and hence the halos of both the liquids appear in the diffraction pattern, though with greater diffuseness. Meyer has distinguished these two types as emulsions and non-emulsions. According to him, the ability to give a new spacing on mixing may be taken as a good test of the perfect miscibility of two liquids. It is not easy to comprehend this state of affairs unless we assume a kind of *loose association* within the mixture between the opposite kinds of molecules. This may occur between groups of opposite kinds of molecules or between opposite molecules forming together into groups. The former of these alternatives seems to be more probable because of the following reason. This offers an interesting transition between miscible and non-miscible liquids. By increasing the number of molecules in each group, we arrive at the case of non-miscible liquids. While by decreasing the number and hence increasing the intermolecular forces, we arrive at the case of what is rigorously called association.

It is interesting to picture the grouping in a liquid B as another liquid A is gradually added to it. At low concentrations, the molecules of A spread throughout the liquid B as gas molecules do in space. This point is verified by the experiments of Krishnamurti who finds greater diffuse scattering at small angles for low concentrations. As more molecules enter into the liquid, the molecules of A arrange themselves into groups characteristic of liquid A. At this stage we get the halos of both the liquids in the diffraction

[23] Krishnamurti, Ind. Jour. Phys. **2**, 501 (1928) ; **3**, 307 (1928), **3**, 331 (1929), **3**, 507 1929).

[24] A. W. Meyer, Phys. Rev., **38**, 1083 (1931).

pattern. This is evident from some published curves of Meyer. As the concentration of liquid A is increased further, there is a kind of loose association between the groups so that a new planar spacing is obtained. Both Krishnamurti and Meyer have recorded that this resultant halo is more diffuse which is exactly what one should expect under these conditions.

This kind of breaking into groups and loose association will not produce any change in the specific susceptibility as calculated by the additive law. This is exactly what we have found in this investigation.

There is further evidence to show that breaking of groups does not produce any change of susceptibility. As the temperature of a liquid is increased, X-ray haloes show that there is a progressive breaking of the groups.[25] Variation of the susceptibility of an ordinary liquid with temperature has been studied by Mathur[26] and by one of us with Mr. Narayanaswami Iyer in this laboratory.[27] Generally the susceptibility is constant unless as in the case of nitrobenzene there is a large association at ordinary temperatures. Vaidyanathan's[28] work also shows that there is no large variation of the susceptibility as the liquid is transformed into the vapour state at the boiling point. It will be interesting to study the susceptibility of liquids at different temperatures right up to the critical temperature. These experiments have been undertaken in this laboratory.

Work with other liquid mixtures by môre sensitive methods is in progress.

[25] Ramasubramanian, Ind. Jour. Phys., **3**, 137 (1928); V. I. Vaidyanathan, Ind. Jour. Phys., **3**, 391 (1929) ; **5**, 501 (1930).

[26] R. N. Mathur, Ind. Jour. Phys., **6**, 207 (1931).

[27] As yet unpublished.

[28] Vaidyanathan, Phys. Rev., **30**, 512 (1927) ; Ind. Jour. Phys., **2**, 135 (1927).