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Magnetic Susceptibilities of Chloroform Mixtures

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Magnetic susceptibilities of nine typical liquid mixtures were determined as a function of concentration. Deviations from an additive law were observed for these mixtures of chloroform with triethylamine, aniline, pyridine, α-picoline, 2,4-lutidine, diphenyl ether, toluene, nitrobenzene and chlorobenzene. The observed deviations are explained on the basis of hydrogen bond formation.

Early experimental work regarding the effect of hydrogen bond formation on magnetic susceptibility has been done by Angus and Hill,[1] Venkataramaiah,[2] Varadachari,[3] and Rumpf and Seguin.[4] Milligan and Whitehurst[5] reviewed the work up to 1952, and interpreted their own measurements of magnetic properties of hydrogen-bonding substances namely, water, propanol and acetic acid absorbed on silica gel with the assumption that hydrogen bonding decreases diamagnetism. Recent studies of Venkateswarlu and Sriraman[6] and

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[1] W. R. Angus and W. K. Hill, *Trans. Faraday Soc.*, **36**, 923 (1940).

[2] H. S. Venkataramaiah, *J. Mysore Univ. Sect. B.*, Contrib. 10, in Phys. 3, Part 4, 19 (1942).

[3] S. V. Ananthakrishnan and P. S. Varadachari, *Proc. Indian Acad. Sci., Sect. A*, **20**, 128 (1944).

[4] P. Rumpf and M. Seguin, *Bull. Soc. Chim. Fr.*, **1949**, D 366; **1950**, 177, 542.

[5] W. O. Milligan and H. B. Whitehurst, *J. Phys. Chem.*, **56**, 1073 (1952).

[6] K. Venkateswarlu and S. Sriraman, *Trans. Faraday Soc.*, **53**, 433 (1957).

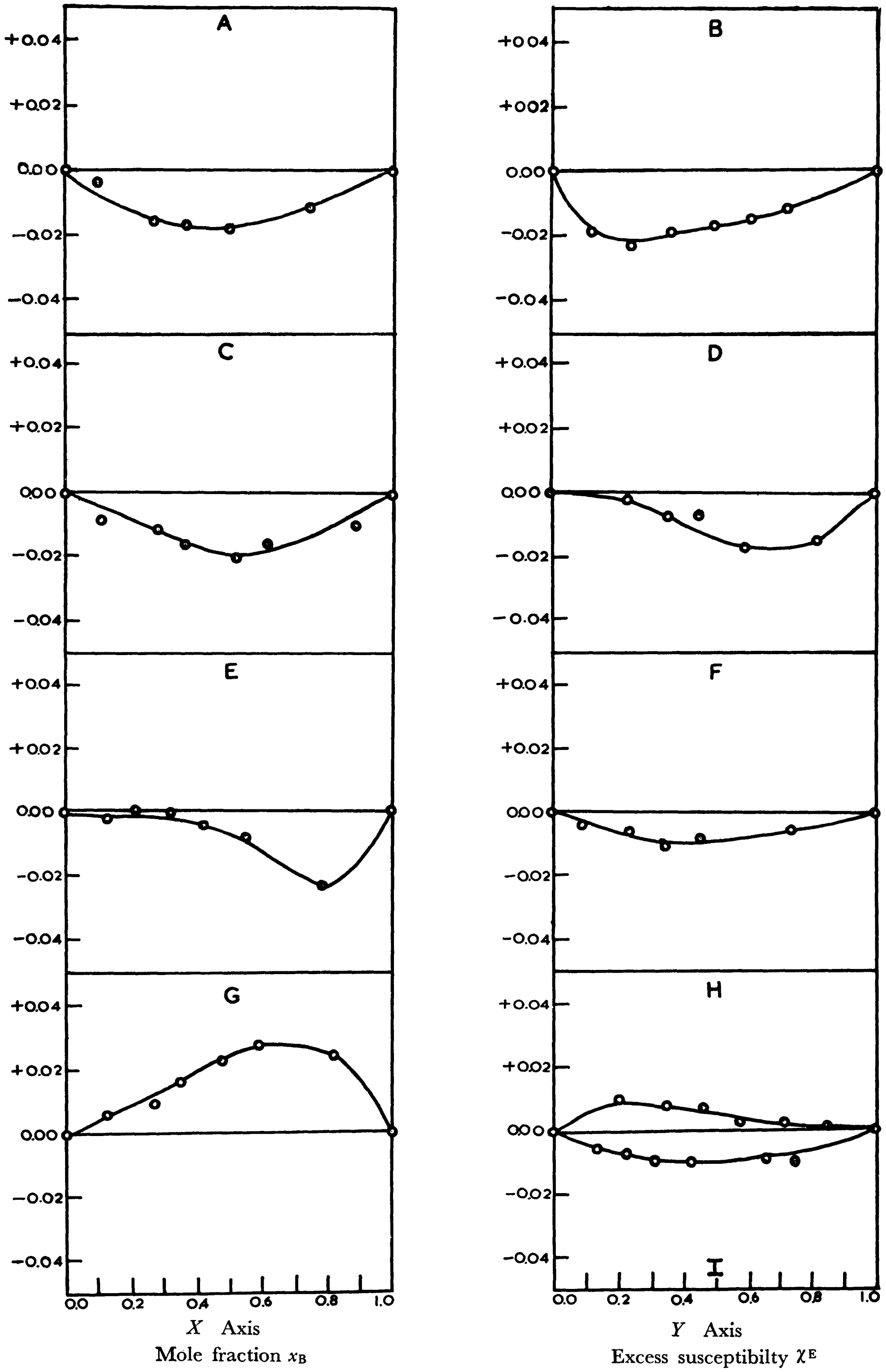

Fig. 1. Excess susceptibility, χ^E *vs.* Mole fraction of second component, x_B.
A, triethylamine B, aniline C, pyridine
D, α-picoline E, 2,4-lutidine F, diphenyl ether
G, toluene H, nitrobenzene I, chlorobenzene

Deshpande and Pathki[7] confirm the above view.

Experimental

Mixtures were prepared by mixing weighed amounts of pure components. Pure components were previously distilled in an all-glass apparatus. The specific susceptibilities were measured using a standard Gouy balance. The Gouy force ranged from 20 to 30 mg and the accuracy of its determination was estimated to be 0.05 mg. The magnetic susceptibilities of standard liquids were determined as a check and results were in good agreement with the accepted values. Water was used as a reference liquid in all measurements with $\chi=-0.720\times10^{-6}$. Densities were determined by the pycnometer method.

Results and Discussion

The results are presented in the figure where the excess susceptibility, χ^{E}, defined as the difference between the experimental value and linear law value, is represented as a function of molecular concentration x_{B} of the second component, the concentration of the first component (chloroform) being x_{A}.

Before a discussion of the results in the light of hydrogen bond formation it is necessary to find whether there would be any effect of hydrogen bond on susceptibility. For this, we use the explanations given by Pople, Bernstein and Schneider.[8]

In the electrostatic picture of hydrogen bond[9] of the type X–H---Y, Y system is superposed on the X–H bond to produce a strong electric field which attracts the partially screened proton of the X–H bond. Consequently, the proton of the hydrogen bond will be drawn away from its own bonding electrons. This produces a distortion in the charge distribution round H. The screening, not being spherically symmetrical, has to be expressed in terms of an appropriate tensor. The components of this tensor will then affect the values of magnetic susceptibility of the hydrogen and endow it with an anisotropic character. The principal components of susceptibility parallel and perpendicular to the bond can be written as

$$\chi_{\parallel}=\chi_0+\eta_{\parallel}E^2$$

$$\chi_{\perp}=\chi_0+\eta_{\perp}E^2$$

where χ_0 is the value of the susceptibility in the free state, E is the electric field at the hydrogen due to the donor electrons. The values of η's are given by

$$\eta_{\parallel}=-\frac{159a^6}{16mc^2};\quad \eta_{\perp}=-\frac{797a^6}{48mc^2}$$

where a is the radius of the Bohr orbit. The mean susceptibility value is given by

$$\chi=\chi_0+\frac{1}{3}(\eta_{\parallel}+2\eta_{\perp})E^2$$

Therefore, the fractional change in susceptibility per hydrogen atom is

$$\left|\frac{\chi-\chi_0}{\chi_0}\right|=\left|\frac{\Delta\chi_0}{\chi_0}\right|=28.76\ \frac{a^4}{c^2}E^2=28.76\times E_{au}^2$$

where E_{au} is the value of electric field expressed in atomic units. A rough estimate of this change can be made by considering a O–H---O bond. Calculations carried out by Pople[10] show that $E=4\times10^5$ e.s.u. or 0.024 au. It therefore leads to a value of (−0.017) for $\left|\frac{\Delta\chi}{\chi_0}\right|$ *i. e.*, a lowering of roughly 2%. In the present investigations, values of χ^{E} of this order of magnitude have been observed.

There is still another aspect of the hydrogen bonding refered to as "ring effect" which arises in the case of mixtures of chloroform with certain aromatic compounds (Pople,[11] Reeves and Schneider[12]).

The mixtures of chloroform with different liquids are discussed one by one. In the case of triethylamine the electronegative 'N' leads to the formation of C–H---N bond with chloroform. There is considerable evidence in support of this based on PMR and infrared absorption[13,14] studies of these mixtures. Such a hydrogen bond formation usually results in large negative excess function. Our observations are consistent with this.

The nitrogen in aniline has two attached hydrogen atoms and by itself is an electron donor. There is a possibility of bonding between N and C–H bond of the chloroform. This is consistent with evidence from infrared absorption studies.[15,16] Our measurements show a large negative value for χ^{E}.

Consider the solution of chloroform with pyridine. There is evidence for hydrogen bond formation between chloroform and this strong base.[17] The nitrogen is highly electronegative. Consistent with

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[7] V. T. Deshpande and S. Pathki, *ibid.*, **58**, 2134 (1962).

[8] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw Hill, New York (1959).

[9] J. A. Pople, "Hydrogen Bonding" Symposium on Hydrogen Bonding at Lubljana, ed. by D. Hadzi, Pergamon Press, London (1959), p. 73.

[10] J. A. Pople, *ibid.*, p. 74.

[11] J. A. Pople, *J. Chem. Phys.*, **24**, 1111 (1956).

[12] L. W. Reeves and W. G. Schneider, *Can. J. Chem.*, **35**, 251 (1957).

[13] G. M. Barrow and E. A. Yerger, *J. Amer. Chem. Soc.*, **76**, 5247 (1954).

[14] C. M. Huggins, G. C. Pimental and J. N. Schoolery, *J. Chem. Phys.*, **23**, 1244 (1955).

[15] J. Landauer and H. McConnell, *J. Amer. Chem. Soc.*, **74**, 1221 (1952).

[16] K. C. Medhi and G. S. Kastha, *Indian J. Phys.*, **37**, 139 (1963).

[17] G. C. Pimental and A. L. McClellan, "Hydrogen Bond," Freeman and Coy, San Francisco (1960), p. 199.

this we obtain a large negative value for χ^E.

α-Picoline molecule can be considered to be arising out of the attachment of a methyl group to the pyridine ring in its α-position. In this case also there is evidence from IR studies[18] in favour of hydrogen bonding. The excess value, χ^E is small in our studies, which does not enable us to lay any great stress on it.

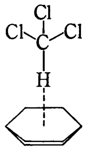
Similar is the case with 2,4-lutidine. There seems to be no chemical or other evidence in support of hydrogen bonding. The possibility of such a bonding is small because of disubstitution by methyl groups in 2 and 4 positions of the pyridine ring. In our studies, we find very small, irregular positive and negative values of χ^E.

In diphenyl ether solutions, we find small progressive deviation and this is attributable to hydrogen bonding. The ether oxygen is highly electronegative and because of this there is a possibility of hydrogen bond formation (type C–H---O). Deviations, however, are small. In the absence of any conclusive evidence, we feel that this may be taken to be a case where there is a large dipolar interaction.

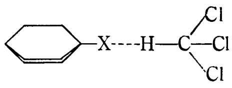
The small negative value of χ^E in the case of 2,4-lutidine, and diphenyl ether mixtures can be explained by invoking a relaxation mechanism associated with hydrogen bonding as has been done by Reddy.[19] Hydrogen bonds are formed and broken in such quick succession that on a macroscopic scale their effect is not perceptible particularly, if the effect is sought to be measured employing a static method of measurement.

Toluene mixtures show a positive deviation, nitrobenzene an almost zero or slight positive deviation, and chlorobenzene a negative deviation. These substances are built round the benzene ring. NMR studies[12] of their mixtures with chloroform show evidence of "ring effect". Taking this "ring effect" into account it is possible to explain the observed trends in χ^E.

The electrons circulating in the aromatic ring have a donor character. The hydrogen in chloroform has an acceptor character. In the mixtures of chloroform with aromatic compounds, chloroform attaches itself to the aromatic ring and forms a bonded complex. There are two positions for such a bonding. The C–H bond in chloroform standing perpendicular to the plane of the ring is called π-bonding and its orientation parallel to the plane of the ring leads to the formation of *n*-bonding.



(π-type)



(*n*-type)

The aromatic ring, unless hindered, orients itself with its plane perpendicular to an external magnetic field. Therefore, the π bonding produces a paramagnetic effect and an *n*-bond which is a normal hydrogen bond produces a diamagnetic effect. The effects of these bondings contribute a corresponding term to the diamagnetic susceptibility of the mixture. The NMR studies cited above show that there is a strong π interaction with toluene, a relatively weak π interaction nitrobenzene and a still weaker one with chlorobenzene.

In the case of toluene mixtures, there is only π interaction and no *n*-interaction because of preferential orientation of chloroform proton above or below the ring. This introduces a paramagnetic contribution and therefore leads to a positive χ^E as observed in these investigations.

Nitrobenzene is a relatively poor π donor and a better *n*-donor. As a result the net deviation (χ^E) is almost zero in the case of nitrobenzene. In the case of chlorobenzene the *n*-interactions are preponderant leading to a negative χ^E.

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18) W. Gordy, *J. Chem. Phys.*, **7**, 163 (1939).

19) K. C. Reddy, Ph. D., Thesis, Sri Venkateswara University (1964).