*The Magnetic Susceptibility of Iodine in Various Solvents**

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According to studies made by Bhatnagar and Lakra[1], iodine dissolved in cyclohexane has a much smaller diamagnetism than it has in other solvents, such as benzene. It seems rather peculiar that cyclohexane is abnormal as a solvent for iodine in view of the fact that both cyclic and aliphatic saturated hydrocarbons are quite normal in their general behavior as solvents. On the other hand, benzene is surely not an indifferent solvent for iodine. As Mulliken[2] has already clearly pointed out, iodine forms a molecular complex with benzene, the latter playing a role of a π donor ($b\pi$) while the former that of a halogenoid σ acceptor ($x\sigma$). By this conception, he could explain the finite electric moment of iodine in benzene and the charge-transfer spectra observed for a number of cases of similar complex formation.

The present writers have therefore undertaken to carry out the measurements of the magnetic susceptibility of iodine in various solvents in order to examine whether it depends upon the kinds of solvents to any appreciable degree, and if so, in what solvents iodine has an abnormal diamagnetism. The diamagnetism of differently colored solutions of iodine has already been studied by Courty[3], who believed that the magnetic susceptibilities of violet and brown solutions of iodine obey the additivity rule, while red and red-brown solutions do not. His results will be discussed critically in the present paper.

Apparatus and Experimental Procedure

A simple Gouy magnetic balance was employed for the determination of magnetic susceptibility at room temperature. The sample tube made of hard glass was symmetrical in form. It was 22 cm. long with a partition in the middle forming two compartments. The one compartment was filled with the solvent, while the solution under investigation was placed in the other compartment. The cross-sectional area of the liquid column amounted to 0.22 cm². The cell was suspended between the poles of a magnet from a semi-microbalance capable of determining weight changes as small as 0.01 mg. The electromagnet could be supplied with a direct current of up to 17 amp. taken from selenium rectifiers, ripples having been removed by means of a system of condensers. The rectifiers were fed from a 200-volt, three-phase alternating current source stabilized with an appropriate voltage stabilizer and led through suitable transformers before it was applied to the rectifiers. The total resistance of the coil of the electromagnet was less than 3 ohms. Each tip of the pole pieces separated by 1.2 cm. had a circular surface plane of 3 cm. in diameter. The resulting magnetic field could be raised up to about 24,000 oersteds.

The magnitude of the downward force f acting on the tube along its length is given by the expression,

$$f=\frac{1}{2}(\kappa-\kappa_a)AH^2=g\Delta w,$$

where κ and κ_a denote respectively the volume susceptibility of the liquid in one compartment and that of the air in the other compartment of the tube. A is the cross-sectional area of the liquid column, g the gravitational constant, and Δw the apparent increase in weight of the tube on application of the magnetic field. The magnetic balance was calibrated with distilled water and its magnetic susceptibility per cubic centimeter, which is practically identical with that per gram, was set equal to -0.720×10^{-6}. The susceptibility κ per unit volume of the solution under investigation was calculated from

$$\frac{\kappa-\kappa_a}{\kappa_o-\kappa_a}=\frac{\Delta w}{\Delta w_o},$$

where the suffix o refers to water used as the standard, and the volume susceptibility of air κ_a was put equal to $+0.0295\times10^{-6}$. For greater accuracy, a differential method was employed, viz., actual measurements were made of $\kappa-\kappa_o$ rather than $\kappa-\kappa_a$. Due correction was made of the force acting on the glass container because of its possible asymmetry by a blank test with the empty tube. The density of each solution was measured in order to convert the susceptibility per unit volume κ into that per unit weight $\chi=\kappa/\rho$.

Materials

Iodine was purified twice by sublimation. Hexane, benzene, toluene, ethyl alcohol, and carbon disulfide used as solvent were prepared according

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* Read before a meeting of the Chemical Society of Japan held on October 14, 1955.

[1] S.S. Bhatnagar and C.L. Lakra, *Indian J. Phys.*, 8, 43 (1933). See also P. W. Selwood, "*Magnetochemistry*," Interscience Publishers, Inc., New York, 1943, p. 66.

[2] R.S. Mulliken, *J. Am. Chem. Soc.*, 72, 600 (1950); 74, 811 (1952); *J. Phys. Chem.*, 56, 801 (1952).

[3] C. Courty, *Compt. rend.*, 204, 1248 (1937); *Bull. soc. chim. France*, 5, 84 (1938).

to the procedure given by Weissberger[4]. Special precaution was taken against the possible contamination of ferromagnetic impurities in the experimental materials.

Results

The diamagnetic susceptibilities of the solutions of iodine in various solvents are plotted against the weight fraction w of the solute in Fig. 1. It will be seen that the experimental points lie on a straight line for each solvent over the whole range of concentrations investigated. In other words, the susceptibility of the solutions χ_{12} obeys a simple formula,

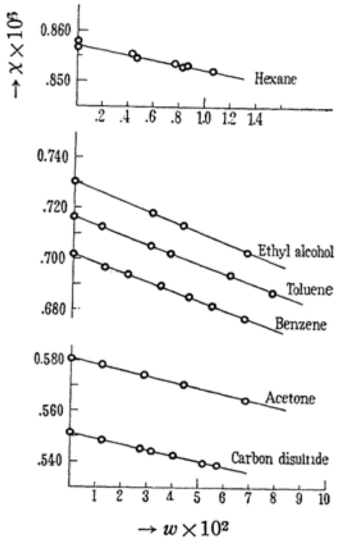

Fig. 1. Dependence of the diamagnetic susceptibilities per gram of solutions of iodine in various solvents upon the weight fraction of the solute.

$$\chi_{12}=\chi_1(1-w)+\chi_2 w,$$

where suffixes 1 and 2 refer to the solvent and the solute respectively. The susceptibility of iodine in various solvents could be evaluated from the slope of the straight lines and are given in Table I.

TABLE I

MAGNETIC SUSCEPTIBILITY PER GRAM OF IODINE IN VARIOUS SOLVENTS

Solvent	$\chi\times10^6$	Bhatnagar	Color
Hexane	−0.363		violet
Cyclohexane		−0.35	violet
Carbon disulfide	−0.337	−0.50	violet
Benzene	−0.334	−0.51	red
Toluene	−0.341		red
Ethyl alcohol	−0.329		brown
Acetone	−0.344		brown
(Iodine crystal)	−0.350∼0.36		

The accuracy of the magnetic susceptibility of a solute depends upon the precision of the measurement of magnetic susceptibilities of the solutions as well as on the concentration range available. The probable error of the present data is estimated to be less than a few percent except that in hexane which may amount to several percent owing to the small solubility. The solubility of iodine in cyclohexane is almost as small as in hexane.

The susceptibility* of iodine in crystalline state is reported to be −0.36[5] or −0.350[6] at room temperature.

Discussion

The present authors have found no such remarkable dependence of the susceptibility upon solvents as has been reported by Bhatnagar and Lakra and by Courty. And yet a slightly lower value of susceptibility was observed for all employed solvents other than hexane in which iodine assumes a susceptibility value practically identical with that in a crystal.

Bhatnagar and Lakra[1] using a modified Quincke's method obtained the susceptibility values given in the third column of Table I. The striking difference between their results and the present writers' is that Bhatnagar and Lakra found a very high diamagnetism in benzene and in carbon disulfide while the present writers did not. As is mentioned later, one has good reason to believe it is unlikely that the diamagnetism of iodine in solutions is greater than that in pure phase.

Courty[2] used the following solvents for dissolving iodine: carbon tetrachloride, chloroform, and carbon disulfide (violet solutions), ethyl ether (brown solution), and benzene and toluene (red solutions). He found an increasing deviation from the additivity rule as the color changed from violet into red. The additivity of magnetic susceptibility implies two points, first the linear dependence of the susceptibility per unit weight of the solution upon the weight fraction of the solute and second the identity of the susceptibility of the solute in solutions with that of the pure phase. As regards the first, the present writers' data are in conformity for all the solvents employed. Courty's experimental points, on the other hand, are scattered about the respective straight lines to such a great extent that his conclusions concerning the additivity rule seem difficult to be accepted. As to the second point, the

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[4] A. Weissberger and E. Proskauer, "Organic Solvents", Oxford at the Clarendon Press, 1935.

* Susceptibility values are given in unit 10^{-6}.

[5] International Critical Tables, VI.

[6] S. R. Rao and H. S. Venkataramiah, *Current Sci.* (India), **14**, 195 (1945); *Chem. Abstr.*, **40**, 258 (1946).

diamagnetism of iodine which was found by the present writers in solutions other than hexane solution is slightly smaller than that in hexane or in pure phase. Even a violet-colored carbon disulfide solution gave a result nearly identical with that in benzene solution. The deviations found by Courty for brown and red solutions are of the same sign as in the present investigation but much greater in magnitude, whereas the deviations found by Bhatnagar and Lakra for benzene and carbon disulfide are of the opposite sign. They are also great, as has already been mentioned. In order to lend support to the present writers' results, the following theoretical calculation was carried out of the change of diamagnetism of iodine on dissolution in benzene.

Benesi and Hildebrand[7], using spectroscopic methods, have shown definitely that benzene and iodine form a 1:1 complex of considerable stability. They found that 60 percent of iodine dissolved in benzene is present in the complex. On the other hand, the close agreement in form and intensity between the spectrum of iodine in the vapor state and in violet solutions indicates that complexes are not formed in these.

Mulliken[2] developed a theory of molecular complexes based on the concept of charge-transfer. He discussed the structure of the complex of iodine with benzene (Bz) in terms of resonance between a predominant no-bond structure (Bz, I_2) and a small admixture of the type (Bz^+–I_2^-). From Fairbrother's[8] data of the moment of iodine in benzene and the overlap integral estimated for the most probable model of the complex, Mulliken calculated the ionic character of the complex in the ground state to be approximately 2.8 percent. The susceptibility of the complex in the hypothetical no-bond state may be assumed to be equal to the sum of the susceptibilities of its component parts. The diamagnetism of the dative structure was estimated in the following way. The principal susceptibility of benzene normal to the plane of the ring ($K_3=-91.2$) is more than twice that in the plane ($K_1=K_2=-37.3$)[9]. The loss of one out of six π-electrons of benzene to form Bz^+ will lead to the decrease of molal diamagnetism of the order of magnitude $(1/3)(1/6)\Delta K=3.0$, where the factor 1/3 was introduced to take into account all the possible orientations of the plane of the benzene ring in space. It would be more desirable to calculate the diamagnetic contribution of an electron in the highest occupied orbital of a benzene molecule by means of molecular orbital treatment. However, noticeable improvement is not to be expected in view of the uncertainty of other data[10]. The increase of diamagnetism of I_2 due to the gain of an electron to form I_2^- may be approximated by the difference between the diamagnetism of I^- and Pascal's constant for I, $50.6-44.6=6.0$*. Therefore with due regard to the constitutive correction constant (+4.1*) for C–I bond formation, the increase of molal susceptibility of the complex (Bz^+–I_2^-) over that of (Bz, I_2), i. e., the decrease of diamagnetism was calculated as $3.0-6.0+4.1=1.1$. It is doubtful whether this figure is really significant in view of the accumulated errors for a small difference. However, it would seem that the decrease of diamagnetism of iodine on dissolution in benzene should be very small, if at all, because the contribution of the dative structure is only 2.8 percent and in addition only 60 percent of iodine is present in the complex.

Summary

The diamagnetic susceptibility per gram of iodine in solutions of various solvents was measured with a Gouy magnetic balance at room temperature. The value -0.363×10^{-6} in hexane solution was practically identical with that of iodine in pure phase. The values of diamagnetism of iodine in carbon disulfide, benzene, toluene, ethyl alcohol, and acetone ranging from -0.329 to -0.341 are only slightly smaller than the value in hexane, in disagreement with the data found in literatures. A qualitative support for the present writers' result was afforded by theoretical considerations based on Mulliken's theory of complexes formed in accordance with the mechanism of electron transfer from a donor molecule to an acceptor.

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[7] H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **70**, 2382 (1948); **71**, 2703 (1949).

[8] F. Fairbrother, *Nature*, **160**, 87 (1947); *J. Chem. Soc.*, **1948**, 1051.

[9] K. Lonsdale and K. S. Krishnan, *Proc. Roy. Soc. London*, **A 156**, 597 (1936).

[10] S. Fujii and S. Shida, This Bulletin, **24**, 242 (1951).

* These numerical data were taken from Selwood. loc. cit.