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The Magnetic Properties of Iodine in Different Solvents.

BY

S. S. BHATNAGAR AND C. L. LAKRA.

The susceptibilities of ions whether paramagnetic or diamagnetic in nature are as a general rule determined from measurements on solutions of polar salts by allowing for the susceptibility of water. If χ, χ_s and χ_ω be the susceptibilities of the solution, of the salt and of water and C_s the concentration of the salt then

$$\chi = C_s \, \chi_s + (1 - C_s) \, \chi_\omega.$$

This relation is found to hold although slight deviations have been observed owing to the influence of the solvent on the solute. The exact nature of this interaction cannot be inferred from the magnetic data. We have however, studied the magnetic properties of iodine in such solvents as benzene, cyclo-hexane and carbon disulphide and it appears to us that the results obtained are capable of rational interpretation on magnetic data. Interest in this study is further enhanced by the fact that the conclusions arrived at find excellent confirmation from measurements on the electric moments of iodine in these solvents.

The magnetic properties of iodine in solutions were measured by means of a modified Bauer and Piccard method which

has been described in a previous paper,[1] the only difference from this arrangement being that the double jacketted tube was further improved to secure uniformity of temperature and a bigger electromagnet was employed so that the meniscus changes for water with a current of 5 amps. in the electromagnet were never less than 1150 divisions of the scale of the micrometer eyepiece and the accuracy of measurements is of the order of 0·0001 cm.

Scrupulous care is required regarding the cleanliness of the tube, and the readings were taken at constant temperatures regulated by allowing water from a thermostat to flow in the double-jacketted vessel. The values of the magnetic susceptibility χ were calculated by the equation :

$$\chi = \frac{2\theta g}{H^2} + \chi_o \frac{\rho_o}{\rho}$$

where
χ = specific susceptibility of the liquid.
χ_o = specific susceptibility of air.
$\rho_o '$ = density of air.
ρ = density of the liquid.
θ = displacement of the meniscus.

The apparatus was standardised with respect to
Water   = -0.72×10^{-6} at 20°C.
Cyclo-hexane = -0.811×10^{-6} at 15°C.
Carbon disul-
     phide   = -0.55×10^{-6} at 10°C.

From the value of χ of the solution the value of the iodine was calculated by the following equation :

$$\chi \text{ salt} = \frac{\chi \text{ solution} - (1 - \frac{p}{100}) \chi \text{ solvent}}{\frac{p}{100}}$$

where p = percent. by weight of the pure salt in the solution.

[1] Phil. Mag. (7), 10, 101—9, 1930.

The results obtained are shown in the following table :—

TABLE I.

Solvent.	χ for iodine.	Temperature.
Benzene.	-0.51×10^{-6}	15°C.
Cyclohexane.	-0.35×10^{-6}	15°C.
Carbon disulphide.	-0.50 to -0.51×10^{-6}	10°C.

The amount of iodine corresponded to a concentration from 0.4147 to 2.79 gms. in 50 c. c. of benzene, but the value of χ for iodine calculated was always within $\pm 8\%$ of the figure -0.51×10^{-6}, showing that the concentration had only slight effect on the susceptibility of iodine. The concentrations in cyclohexane and carbon disulphide were 0.4231 gm. and 0.4202 gm. respectively in 50 c. c. of the solvent. Even after applying a correction for the change of χ of the solvent with temperature the calculated value of χ for iodine showed a slight change on heating. These results will be discussed in a fuller paper later, but the interesting point which emerges is that iodine shows a value of specific susceptibility in the neighbourhood of -0.51×10^{-6} when dissolved in benzene and carbon disulphide and a value of -0.35×10^{-6} when dissolved in cyclo-hexane.

The value of -0.35×10^{-6} for the specific magnetic susceptibility of iodine in the solid state is in excellent agreement with the values $(-0.35_5, -0.35 \times 10^{-6})$ due to Curie and Honda and his co-workers as given in the International Critical Tables, Vol. VI, p. 335. It shows in a most convincing manner that when dissolved in cyclo-hexane the iodine does not lose its characteristic elemental character. Such, however, is not the case in benzene and carbon disulphide. If we multiply by the atomic weight the values of χ for iodine as obtained from solution data of these two solvents, we obtain

for gram ionic susceptibility of iodine the values of 64·7 and 63·4 respectively.

It is interesting to compare the values so obtained with the latest theoretical and experimental values of iodine in the ionic state. The results have been gathered together in Table II.

TABLE II.

Gram Ionic Susceptibilities. $-\chi_A \times 10^6$.

Ion.	Theoretical values.			Experimental values.		
	Pauling.	Angus.	Slater.	Carbon di-sulphide.	Benzene.	Cyclo-hexane.
I⁻	80	55·32	59·8	63·4—64·7	64·7	44·42

These results assume importance when they are compared with the dipole moments of iodine. Briegleb[1] has recently observed that iodine has a dipole moment of $1·2 \times 10^{-18}$ in carbon disulphide and in benzene solutions while in hexane and cyclo-hexane it has no permanent dipole moment. It implies that in iodine dissolved in benzene and carbon disulphide the electron pair which is shared between the two atoms tends to be drawn more towards one atom than to the other showing a tendency for iodine to ionise in these solvents. The values of gram ionic magnetic susceptibilities are in fair accord with the theoretical values of Slater. This fact points conclusively in favour of the ionisation of iodine in benzene and carbon disulphide. In cyclohexane there is no ionisation and the calculated specific susceptibility $-0·35 \times 10^{-6}$ agrees with the experimental value of χ for iodine.

[1] "Recent Advances in Physical Chemistry," by S. Glasstone (Churchill's publication), 1931.

Incidentally it is interesting to note that Brindley[1] and Kido[2] also find that Slater's method of calculating charge distribution gives susceptibilities in better agreement with experiment than those calculated by the Pauling or the Hartree method.

UNIVERSITY CHEMICAL LABORATORIES,
UNIVERSITY OF THE PANJAB,
LAHORE.

[1] Phil. Mag., *11*, 786. (1931.)

[2] Sc. Reports Tohoku Imp. Univ , Vol. 21, 1, (1932).