[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RICE INSTITUTE]

THE PHOTOMAGNETIC PROPERTIES OF THE SILVER HALIDES

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A number of the photochemical properties of the silver halides indicate that the molecules of the solid salts are made more polar by absorption of visible radiation. For example, the salts become better conductors of electricity on illumination, an occurrence which must be parallel to an increase in specific inductive capacity. The changes in potential of the silver halide electrodes in light may also be explained on the assumption that the silver ions are loosened from the halide ions by the absorption of light, thus producing a greater concentration of these ions in solution than would be maintained in equilibrium with the solid salt in the dark.[2]

This apparent increase in the electric polarity of the molecule due to absorption of light suggested the possibility of a simultaneous change in the magnetic permeability. Acting on this suggestion the phenomenon which may be called a "photomagnetic effect" was discovered.

Since the new ideas of the chemical bond and molecular structure advanced by Prof. Lewis have been supported to some extent by magnetic properties, some knowledge of the influence of light on these properties may prove useful. It will certainly assist in understanding the nature of photochemical action.

Experimental Method

The purpose of this investigation was to determine in a qualitative way the effect of light on the magnetic permeabilities of the silver halides. These experiments will be followed by more quantitative ones as soon as a satisfactory method is perfected.

The experimental principle was simple. A needle of the silver halide to be observed was suspended from a quartz fiber between the poles of an electromagnet and the deflection of the needle or torque produced by the magnetic field in the dark was compared with that obtained when the needle was illuminated with a beam of white light.

The three salts, silver chloride, bromide and iodide, were prepared by precipitation from silver nitrate solution with a slight excess of the potassium halide. The salts were dried and fused. The needles were prepared by pouring the molten salts into a crevice between two glass plates and removing the plates as soon as the salts had solidified. They were approximately 0.5 mm. thick, 2.0 mm. wide and 3.0 cm. long. They were fastened with wax at the mid-point to the lower end of a fine glass rod

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[1] National Research Fellow in Chemistry.

[2] Garrison, *J. Phys. Chem.*, **28**, 334 (1924).

(0.1 mm. in diameter and 4.0 cm. long) which bore a light mirror at its upper end and was suspended by the quartz fiber.

This suspended system was inclosed in a glass tube having a ground-glass joint to facilitate the replacement of the needle, and a side tube connected to a vacuum pump for removing the air to avoid disturbances due to eddy currents. A vacuum of approximately 0.1 mm. of mercury was maintained during the observations. The tube was provided with a plane surface window through which the motions of the suspended system could be observed in the mirror by use of a telescope and scale.

The needle could be illuminated through the walls of the glass tube with light from a 500-candle power tungsten lamp placed at a distance of 25 cm. A 12mm. water filter was interposed to absorb the long wave-length heat rays.

The tube was placed between the poles of an electromagnet so that the needle was situated in the field making an angle of 45° with the lines of force. This made it possible to compare the properties of both paramagnetic and diamagnetic needles under almost identical conditions.

Experimental Results

The magnetic properties of the halides were found to vary considerably. All the samples of silver chloride were slightly diamagnetic; the bromide and iodide were slightly paramagnetic. Impurities and the extent to which the salts decomposed on fusing and by photochemical action apparently influenced the permeability.

In every case the permeability of the silver salt was increased by illumination. The diamagnetic chloride was less diamagnetic in light and the paramagnetic bromide and iodide were more paramagnetic in light. The relative magnitude of the effect may be seen from Table I.

TABLE I

THE RELATIVE PHOTOMAGNETIC EFFECTS OF THE SILVER HALIDES

Substance	E.m.f. on magnet Volts	Deflection in dark	Deflection in light	Deflection in heat rays
AgCl	1.2	D[a] 4.1	D 3.2	D 0.5
AgCl	1.15	D 3.85	D 3.25	D 2.5
AgBr	1.2	P[b] 3.8	P 4.1	P 4.8
AgI	1.12	P 9.3	P 9.55	P 10.2

[a] D, diamagnetic.

[b] P, paramagnetic.

The magnetic field was measured with a fluxmeter when the e.m.f. at the terminals of the electromagnet was 1.2 volts and found to be 200 gauss. It will be noticed that the first sample of the silver chloride was twisted by this field through 4.1 scale divisions in a direction indicating that it was diamagnetic. When the light was turned on, the deflection was diminished to 3.2 divisions. The change was instantaneous and on extinguishing the light the original deflection was obtained. The changes were so rapid that the needles could be made to swing violently back and forth by turning the light off and on at regular intervals timed by the natural period of the suspension.

A second sample of silver chloride is included in the table to show the relative magnitude of the variations.

The silver bromide was paramagnetic to the extent of 3.8 divisions and the paramagnetism was increased to 4.0 divisions on illumination.

The silver iodide was as a rule more paramagnetic than the other salts and influenced by light to the smallest extent.

A more decided increase in the permeability was obtained by a longer exposure of the needle to heat rays admitted by removing the water screen. The changes were slower in this case and are thus not distinguishable from those caused by a rise in temperature. The deflections given in the last column of the table were obtained after two minutes of illumination without the water filter. The effect on the salts did not disappear immediately after illumination as it did in the case of visible light only, but the samples required ten to fifteen minutes to return to the original condition.

Discussion

In Langevin's theory[3] of para- and diamagnetism the molecule is supposed to contain electron orbits each equivalent to a small magnet. The elementary magnets are supposed to be fixed in the molecule and not free to rotate in a magnetic field, nor are they influenced by temperature. As a consequence of the electromagnetic theory, the effect of a magnetic field is to alter the shape of the orbits in such a manner as to produce the phenomenon of diamagnetism. When, however, the molecule as a whole has a resultant magnetic moment and is free to rotate, paramagnetism will overshadow the small diamagnetic effect of the change in the individual orbits.

The theory explains the general rule that the permeability of a paramagnetic substance decreases with increasing temperature, for increased molecular agitation would tend to decrease the average amount of dipole orientation. On the other hand, the permeability of a typical diamagnetic substance would be independent of the temperature.

It is immediately apparent that the silver halides do not conform to this generalization. The permeability of the diamagnetic silver chloride as well as the paramagnetic bromide and iodide is increased rather than decreased by rays that should augment molecular agitation. This does not prevent the application of the theory of Langevin but necessitates additional assumptions.

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[3] Langevin, *Compt. rend.*, **139**, 1204 (1904); *Ann. chim. phys.*, **5**, 70 (1905).

The ideas of molecular structure advanced by Lewis[4] are best adapted to explain the photochemical and photomagnetic properties of the silver halides. According to this theory, silver chloride has the structure $\mathrm{Ag}\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$ where Ag represents the silver kernel having the electron configuration 2, 8, 18, 18, and Cl represents the chlorine kernel having the electron configuration 2, 8.

Solid silver chloride is comparatively non-polar, has a very small solubility product in water and is diamagnetic. Thus the arrangement of the electron orbits is such that the magnetic fields are well closed within the molecule.

Its behavior in the photovoltaic cell indicates that silver chloride becomes more soluble in water when it has absorbed light. The salt at the same time becomes a better conductor of electricity. This indicates an increase in electric polarity which may be represented by writing the formula, $\mathrm{Ag}\quad:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$ with the electron doublet forming the chemical bond displaced toward the chlorine. It is probable that this transition from a less polar to a more polar state takes place in steps corresponding to the absorption of quanta.

The molecule in the more polar state has the great magnetic permeability. This may be the result of a readjustment of the electron orbits and increased magnetic moment of the individual ions due to the increased electrostatic forces, or a greater degree of atomic orientation may be possible when the bond between the ions is loosened.

The substitution of a halide of higher atomic weight apparently increases the permeability and decreases the relative magnitude of the photomagnetic effect.

Summary

The influence of light on the magnetic permeabilities of silver chloride, bromide and iodide was investigated in a qualitative way. The salts had been fused and were in the form of needles.

The silver chloride was diamagnetic and the bromide and iodide were slightly paramagnetic. The chloride became less diamagnetic on illumination while the bromide and iodide became more paramagnetic in light. Thus the magnetic permeability of each was increased by the visible radiation.

A rise in temperature by the absorption of heat rays also increases the permeability of each salt, but the changes are slow whereas the effect of light is instantaneous.

It was pointed out that a change in the magnetic permeability would

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[4] Lewis, THIS JOURNAL, **38,** 762 (1916). *Proc. Nat. Acad. Sci.,* **2,** 586 (1916). *Science,* **46,** 297 (1917).

naturally accompany an increase in electrical polarity, an occurrence which is suggested by the fact that the absorption of light causes the halides to be more soluble in water and better conductors of electricity.

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THE VISCOSITY OF LIQUIDS CONTAINING DISSOLVED GASES[1]

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The measurement of the viscosity of liquids containing dissolved gases has been almost entirely neglected. Poiseuille[2] measured the viscosities of a saturated solution of carbon dioxide and of solutions of hydrochloric and hydrobromic acids. Wolfgang Ostwald[3] found that saturated solutions of nitrogen, carbon dioxide and oxygen at 20° had viscosities of 57.18, 56.5 and 55.62, respectively, as compared with 56.2 for pure water, and concluded that these gases had no effect on the viscosity of water.

This investigation was undertaken to determine the influence of dissolved gases on the viscosity of certain liquids.

Experimental Part

Purification of Materials

Organic Solvents.—The substances employed were purified and dried by the usual methods and finally fractionated, the main fractions boiling within a 0.1° interval, or less. The heptane was kindly given by Professor Edward Kremers,[4] who obtained it by distillation of the volatile oils obtained from the oleoresin of *Pinus Jeffreyi*. The distillate thus obtained was freed from resinous materials by saturating the cold solution with hydrogen chloride. After washing with water to remove the hydrogen chloride, sodium was added to remove the last traces of water.

Gases.—The chlorine was prepared from hydrochloric acid and manganese dioxide, washed with a solution of copper sulfate and dried with sulfuric acid. The hydrogen sulfide was prepared from sodium sulfide and purified by passage through water, a 20cm. tube containing iodine and a long calcium chloride tube. The sulfur dioxide was either prepared from sodium bisulfite or taken from a cylinder of the liquefied gas; it was dried and freed from dust particles before using.

Apparatus

Viscometer.—The viscometer used in this work was a modified Ostwald-Washburn instrument.[5] The Bingham viscometer[6] is probably

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[1] The work included in this paper is from the thesis presented by John R. Lewis in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin. The subject of this research was suggested by Professor James H. Walton and the investigation was conducted under his direction.

[2] Poiseuille, *Ann. chim. phys.*, **21,** 76 (1847).

[3] Wo. Ostwald, *Zool. Jahrb. Biol.*, **18,** 12 (1903).

[4] Kremers, *J. Am. Pharm. Assoc.*, **9,** No. 11, 1 (1920).