

## Magnetic Birefringence in Solutions of Sodium Chlorate and Sodium Bromate

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### ABSTRACT.

Sodium chlorate and sodium bromate in aqueous solutions are found to exhibit a feeble magnetic birefringence, negative in sign, and smaller in magnitude than that shown by nitrates, as was predicted by Krishnan from his observations on the magnetic anisotropy of potassium chlorate crystal. (Values are given in Table I.) The optical anisotropy of the chlorate ions, calculated from the magnetic birefringence and Krishnan's data, comes out of the same order of magnitude as is to be expected from the known birefringence of the crystal.

### 1. Introduction.

Apart from the great many organic compounds in which magnetic double refraction has been observed,<sup>1</sup> there are also a few inorganic substances<sup>2</sup> like water, nitric acid and nitrate and nitrite ions in solution which exhibit a magnetic birefringence. The sign of the birefringence is negative in water and positive in the other three mentioned. Raman and Krishnan<sup>3</sup> have shown a correlation between the magnetic birefringence

<sup>1</sup> See Landolt-Bornstein Tabellen, Zweiter Ergänzungsband, p. 913.

<sup>2</sup> Ramanadham, Ind. Jour. Phys., 4, 109 (1929); Haque, C.R., 190, 789 (1930).

<sup>3</sup> Raman and Krishnan, Proc. Roy. Soc., A, 115, 549 (1927).

in nitric acid and the optical and magnetic properties of the nitrate crystals. Recently, while measuring the magnetic susceptibilities of certain crystals in different directions, Krishnan<sup>4</sup> found that whereas in the nitrate crystals, the direction of maximum optical susceptibility nearly coincides with that of the minimum diamagnetic susceptibility, the reverse was seen to be the case for potassium chlorate crystals, the directions of maxima of the two coinciding. This indicated that the chlorate ions in solution should show a magnetic birefringence negative in sign, as opposed to the positive one shown by the nitrate ions.

### 2. Results.

The author tested solutions of sodium chlorate and sodium bromate for magnetic birefringence using the same half-shade analyser to detect and measure the birefringence as he used for the aliphatic liquids,<sup>5</sup> the other experimental arrangement being also the same. The results are given in the table below,  $C_m$  being the relative value of magnetic birefringence on scale acetone = +1.6, i. e., nitrobenzene = +100.

TABLE I.

Solute.	Concentration of the solution.	Concentration in gram. equivalents of the solute.	Density of solution.	Observed $C_m$ of solution.	$C_m$ after correcting for water.
Sodium chlorate.	0.78 gms. per c. c. solution.	$0.75 \times 10^{-2}$ gm. equivalent per c. c. solution.	1.42	$-0.36 \pm .03$	-0.26
Sodium bromate.	0.31 gms. per c. c. solution.	$0.20 \times 10^{-2}$ gm. equivalent per c. c. solution.	1.32	$-0.26 \pm .03$	-0.11

<sup>4</sup> K. S. Krishnan, *Phys. Rev.*, 38, 833 (1931).

<sup>5</sup> S. W. Chinchalkar, *Ind. Jour. Phys.*, 6, 165 (1931).

The last column gives the magnetic birefringence due to chlorate or bromate ions after due correction is made for the water present, from the known concentration and density of the solution and assuming that the correction is proportional to the amount of water present. It is thus seen that the chlorate ions as expected from Krishnan's work, as also the bromate ions, show a negative magnetic birefringence. By comparing the values of  $C_m$  and the concentrations in equivalent weights, it can be seen that the bromate ions exhibit a stronger magnetic birefringence than the chlorate ions. It may be noted that the nitrate ions in a solution of the same equivalent concentration as that of sodium chlorate in the table, would exhibit a magnetic birefringence of the value  $C_m = +0.75$  nearly,<sup>6</sup> being thus in magnitude nearly three times that shown by the chlorate ions.

### 3. Discussion.

To compare the magnetic birefringence data for the chlorate ions with the magnetic and optical properties of the ions in the crystalline state, we take the case of potassium chlorate crystal cited by Krishnan. Potassium chlorate is a monoclinic crystal, but two of the principal refractive indices are very nearly equal, so that for practical purposes, it may be taken to be a uniaxial crystal. Zachariassen has determined its crystal structure and finds that there are two molecules per unit cell so orientated that the planes containing the three oxygen atoms of the  $\text{ClO}_3$  ions are parallel to one another. The direction perpendicular to the plane of the oxygen atoms is the axis of the approximate uniaxial crystal. It is also the direction of the minimum diamagnetic susceptibility, and the magnetic symmetry axis. The chlorine atom is not in the plane of the oxygen atoms. Since the induced

<sup>6</sup> Haque, *loc. cit.*

<sup>7</sup> Zachariassen, *Zeit. f. Cryst.* 71, 801 (1929).

magnetic moments in an ion are too small to affect the neighbouring ions in the crystal, the difference  $(\chi_{11} - \chi_1)$  between the molar magnetic susceptibilities of the crystal along and perpendicular to the symmetry axis will be the sum of those for the individual ions. The optical moments are, however, known to be influenced by the neighbouring atoms and ions. Hence taking the magnetic susceptibility differences of the ions from the data for the crystal, and the experimental value of the magnetic birefringence, we can calculate on Langevin's theory the difference in the optical susceptibility of the chlorate ion in solution in the two directions, and compare it with the value found from the refractivities of the crystal. This is done below.

According to Langevin's theory,<sup>8</sup> the formula for the Cotton-Mouton constant of magnetic birefringence can be put in the form

$$C_m = \frac{(n^2 + 2)^2 \nu}{135n\lambda^2 T} \left[ (A - B)(A' - B') + (B - C)(B' - C') + (C - A)(C' - A') \right] \quad (i)$$

where A, B, C, are the optical moments induced in a molecule by a unit electric field of the incident light wave acting along the three mutually perpendicular directions of the optical ellipsoid of the molecule, A', B', C', are the magnetic moments induced by a unit magnetic field along the same three directions, and  $\nu$  is the number of molecules per c. c. In our case  $n$  would be the refractive index contributed by the chlorate ions, which can be calculated from the refractivity data for those ions. Also for these ions, if the axis of symmetry be taken to be the direction of A, then  $B' = C'$ , and

$$(A' - B') = \frac{\chi_{11} - \chi_1}{N} \quad (ii)$$

where  $\chi_{11}$  and  $\chi_1$  are the molar diamagnetic susceptibilities along and perpendicular to the axis of symmetry and N is the

<sup>8</sup> Debye, Handbuch der Radiologie, Bd. VI, p. 769.

Avogadro number. Taking  $(\chi_{11} - \chi_1)$  from Krishnan's data and the experimental value of  $C_m$ , and remembering that  $B=C$ , equation (i) gives the value of  $(A-B)$ ; thence an equation analogous to (ii) would give

$$N(A-B) = R_e - R_o \quad (iii)$$

where  $R_e$  and  $R_o$  are the gram. molecular refractivities along and perpendicular to the axis. The value of  $(R_e - R_o)$  calculated in this way from equation (i) comes to  $-2.41 \pm 0.25$ .  $(R_e - R_o)$  for  $KClO_3$  crystal is  $-2.12$  from the refractivity data given in the International Critical Tables,<sup>9</sup> and  $-2.97$  from the data of Porter.<sup>10</sup> These are in fair agreement with the value obtained above, considering the divergence between the two crystal values, and the relative error involved in the measurement of the constant of magnetic birefringence.

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<sup>9</sup> Int. Crit. Tables. Vol. 1, p. 169.

<sup>10</sup> Quoted in Landolt Bornstein Tabellen, Zweiter Ergänzungsband, p. 780.