

# THE MAGNETO-OPTIC ANOMALY OF ELECTROLYTES IN AQUEOUS SOLUTION—II

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## 1. INTRODUCTION

IN a preliminary study by the author on the magneto-optic anomaly in electrolytic solutions (Ramaseshan, 1948) it was noticed that solutions of the alkali halides had values of the anomaly greater than that for water. On the other hand the presence of sodium chlorate and the alums in water always decreased its  $\gamma$  value. This difference in behaviour between the simple alkali halide ion and the other more complicated ones induced the author to undertake a systematic measurement of the magneto-optic and optical constants of a large number of ionic solutions. In a previous paper (1950) the results obtained with seventeen univalent halide solutions have been reported. This paper gives the results obtained with other ionic solutions especially those containing ions with covalent linkages in them such as nitrates, sulphates, chlorates, bromates, iodates, etc. Amongst the substances that have been studied are 13 halides, 13 nitrates, 8 sulphates, 5 hydroxides, 9 chlorates, bromates and iodates, of monovalent and divalent elements. From the measured values of the Faraday effect and dispersion in these solutions the magneto-optic anomaly has been evaluated. The ionic rotations have also been computed. The last part of the paper gives the values of the magneto-optic anomaly of gases and vapours calculated from data obtained from Landolt and Bornstein's tables.

## 2. RESULTS

The magnetic rotation of the different solutions were measured for  $\lambda 5461$  (Hg green) with water as the standard substance. The refractive indices were measured for  $\lambda 5893$ ,  $\lambda 5461$  and  $\lambda 4358$ . The experimental methods used have already been described in the previous communications by the author. The specific rotations of the ions in solutions are evaluated from the simple Verdet rule for mixtures.

$$[V_s] = [V_z]x_1 + [V_w]x_2,$$

where  $[V_s]$ ,  $[V_i]$  and  $[V_w]$  are the specific rotation of the solution, ions in solution and water and  $x_1$  and  $x_2$  are the number of grams of the substance and water in 100 grams of the solution. The specific rotation  $[V] = V/d$ , where  $V$  is the Verdet constant and  $d$  is the density and the molecular rotation  $[V]_m = [V] \times M$  where  $M$  is the molecular weight. The magneto-optic anomaly for any solution is calculated from the modified Becquerel formula

$$V = \gamma e/2mc^2. (\lambda dn/d\lambda),$$

where  $dn/d\lambda$  is the dispersion for the solution for the wavelength  $\lambda$  for which the Verdet constant is measured. The solutions were made from purest chemicals. Some of the compounds were prepared in the laboratory. Usually a 4-molar solution was made. Table I gives the optical and magneto-optic constants of water and the other solutions.  $M$  is the molecular weight  $X_1$  and  $X_2$  are the number of grams of substance and water in 100 c.c. of solution,  $d$  is the density,  $n$  the refractive index and  $\Delta n$  is  $n_{5893} - n_{4861}$ ,  $V_{5461}$  is the Verdet constant for the solution for  $\lambda_{5461}$ ,  $[V_i]_M$  is the molecular rotation of the ions in solution and  $\gamma$  is the magneto-optic anomaly.

TABLE I

*Optical and magneto-optic constants for water*

$n_{5893}$	$n_{5461}$	$n_{4861}$	$\Delta n \times 10^5$	$V_{5461}$	100 $\gamma$
1.33239	1.33381	1.33953	714	0.01547'	76

TABLE II

*The optical and magneto-optic constants of univalent nitrates in solution (4-Normal solution)*

	M	$X_1$	$X_2$	$d$	$n_{5893}$	$\Delta n \times 10^5$	$V_{5461} \times 10^5$	$[V_i]_M \times 10$	100 $\gamma$
HNO <sub>3</sub> ..	63.02	25.26	83.20	1.0841	*	895	13.60'	2.10'	53.3
LiNO <sub>3</sub> ..	68.95	27.60	88.42	1.1600	1.35626	887	14.81'	2.85'	58.6
NaNO <sub>3</sub> ..	85.01	34.00	84.94	1.1814	1.36543	867	14.62'	3.70'	59.2
KNO <sub>3</sub> ..	101.11	40.48	80.83	1.2127	1.36621	871	14.40'	4.75'	58.0
NH <sub>4</sub> NO <sub>3</sub>	80.05	32.02	81.44	1.1346	1.36811	883	15.10'	6.30'	60.0
AgNO <sub>3</sub>	169.89	68.00	84.39	1.5234	1.39832	1065	16.94'	9.00'	55.8

\* Absolute value of  $n$  was not determined accurately.

TABLE III

*The optical and magneto-optic constants of sulphates in solution  
(1 Normal)*

	M	X <sub>1</sub>	X <sub>2</sub>	d	n <sub>5893</sub>	Δn × 10 <sup>5</sup>	V <sub>5461</sub> × 10 <sup>3</sup>	[V <sub>i</sub> ] <sub>M</sub> × 10	100γ
H <sub>2</sub> SO <sub>4</sub> ..	98.07	9.80	93.90	1.0370	*	775	15.10'	5.80'	69.2
Li <sub>2</sub> SO <sub>4</sub> ..	109.94	11.00	93.02	1.0402	1.35056	745	15.13'	7.41'	71.3
Na <sub>2</sub> SO <sub>4</sub> ..	142.06	14.20	92.81	1.0662	1.35114	748	15.26'	9.07'	71.6
K <sub>2</sub> SO <sub>4</sub> ..	174.26	17.50	89.16	1.0658	1.35144	756	14.91'	11.22'	69.2
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	132.14	13.20	90.50	1.0371	1.35600	781	15.43'	14.37'	69.3

\* Absolute value of n was not determined accurately.

TABLE IV

*The optical and magneto-optic constants of hydroxides (4 Normal)*

	M	X <sub>1</sub>	X <sub>2</sub>	d	n <sub>5893</sub>	Δn × 10 <sup>5</sup>	V <sub>5461</sub> × 10 <sup>3</sup>	[V <sub>i</sub> ] <sub>M</sub> × 10	100γ
HOH ..	18.02	..	..	1.0000	1.33239	715	15.47'	2.78'	76
LiOH ..	23.95	9.58	97.74	1.0732	1.36691	788	17.32'	5.50'	77
NaOH ..	40.00	16.00	95.57	1.1157	1.36770	792	17.43'	6.65'	77
KOH ..	56.11	22.44	90.96	1.1340	1.36816	796	17.08'	7.52'	76.8
NH <sub>4</sub> OH*	35.05	3.50	15.66	0.9917	1.33503	730	15.66'	8.60'	76.3

\* 1 Normal solution.

TABLE V

*The optical and magneto-optic constants of chlorates*

	M	X <sub>1</sub>	X <sub>2</sub>	d	n <sub>5893</sub>	Δn × 10 <sup>5</sup>	V <sub>5461</sub> × 10 <sup>3</sup>	[V <sub>i</sub> ] <sub>M</sub> × 10	100γ
HClO <sub>3</sub> ..	84.47	33.78	82.02	1.1580	1.36780	813	15.85'	7.92'	68.4
LiClO <sub>3</sub> ..	90.40	36.36	82.58	1.1894	1.36820	798	16.36'	8.93'	72.0
NaClO <sub>3</sub> ..	106.30	42.52	82.92	1.2544	1.36880	790	16.56'	9.32'	73.6

TABLE VI

The optical and magneto-optic constants of bromates and iodates

	M	X <sub>1</sub>	X <sub>2</sub>	d	n <sub>5893</sub>	Δn × 10 <sup>5</sup>	V <sub>5461</sub> × 10 <sup>3</sup>	[V <sub>z</sub> ] <sub>M</sub> × 10	100γ
HBrO <sub>3</sub> ..	128.93	38.67	77.67	1.1634	..	880	16.65'	15.46'	67.0
NaBrO <sub>3</sub> ..	150.92	45.27	86.74	1.3201	..	890	18.58'	17.18'	73.3
HIO <sub>3</sub> ..	175.93	52.77	88.61	1.4138	1.40150	1051	22.61'	29.75'	75.5
LiIO <sub>3</sub> ..	181.86	54.54	89.04	1.4358	1.40367	1008	21.69'	26.41'	75.5

TABLE VII

The optical and magneto-optic constants of divalent chlorides

	M	X <sub>1</sub>	X <sub>2</sub>	d	n <sub>5893</sub>	Δn × 10 <sup>5</sup>	V <sub>5461</sub> × 10 <sup>3</sup>	[V <sub>z</sub> ] <sub>M</sub> × 10	100γ
CaCl <sub>2</sub> ..	111.0	44.4	78.68	1.2308	†	852	20.85'	26.27'	85.9
SrCl <sub>2</sub> ..	158.55	63.42	63.19	1.2661	1.38549	920	20.14'	27.30'	76.8
BaCl <sub>2</sub> *..	208.28	62.46	62.14	1.2460	1.37643	842	19.04'	30.70'	79.4
MgCl <sub>2</sub> ..	95.24	38.09	76.61	1.1470	1.37751	892	19.80'	25.00'	78.0
ZnCl <sub>2</sub> ..	136.30	54.52	66.96	1.2148	1.39251	933	20.13'	27.80'	75.7
CdCl <sub>2</sub> ..	183.33	73.23	57.10	1.3043	1.39963	951	20.92'	32.10'	77.4

\* 3 Normal solution.

† Accurate value not determined.

TABLE VIII

Magneto-optic constants of divalent bromides

	M	X <sub>1</sub>	V <sub>5461</sub> × 10 <sup>3</sup>	[V <sub>z</sub> ] <sub>M</sub> × 10	100γ
CaBr <sub>2</sub> ..	199.91	79.96	31.22	48.6'	75.2
SrBr <sub>2</sub> ..	247.46	98.98	31.71'	49.7'	76.0
MgBr <sub>2</sub> ..	184.15	73.66	30.84'	46.1'	74.4
ZnBr <sub>2</sub> ..	225.21	90.00	32.00'	49.6'	77.0
CdBr <sub>2</sub> ..	272.24	108.00	33.70'	53.7'	77.9

TABLE IX

*Magneto-optic constants of divalent iodides*

	M	$X_1$	$V_{5461} \times 10^3$	$[V_i]_M \times 10$	100 $\gamma$
ZnI <sub>2</sub> ..	319.2	95.76	32.03'	102.27'	67.8
CdI <sub>2</sub> ..	366.2	109.86	29.06'	106.43'	68.3

TABLE X

*Magneto-optic constants of divalent nitrates (4 Molar solution)*

	$X_1$	$V_{5461} \times 10^3$	$[V_i]_M \times 10$	100 $\gamma$
Ca(NO <sub>3</sub> ) <sub>2</sub> ..	65.64	13.46	5.80'	43.0
Sr(NO <sub>3</sub> ) <sub>2</sub> ..	84.66	13.80'	6.81'	43.3
Ba(NO <sub>3</sub> ) <sub>2</sub> * ..	26.13	15.24'	10.21'	65.1
Mg(NO <sub>3</sub> ) <sub>2</sub> ..	59.33	12.96'	4.16'	43.2
Zn(NO <sub>3</sub> ) <sub>2</sub> ..	75.76	14.37'	7.03'	44.4
Cd(NO <sub>3</sub> ) <sub>2</sub> ..	94.95	16.21'	11.04'	48.7
Pb(NO <sub>3</sub> ) <sub>2</sub> ..	66.24	19.81'	33.00'	50.3

\* 2 Molar Solution.

TABLE XI

*Molecular magnetic rotation of substances*

Substance	$[V_i]_M \times 10$
NaF ..	2.20'
KF ..	3.24'
NH <sub>4</sub> F ..	4.71'
MgSO <sub>4</sub> ..	5.40'
ZnSO <sub>4</sub> ..	8.20'
CdSO <sub>4</sub> ..	11.90'
HgCl <sub>2</sub> ..	37.58'
HgI <sub>2</sub> * ..	129.84'
Mg(BrO <sub>3</sub> ) <sub>2</sub> ..	35.87'
Zn(BrO <sub>3</sub> ) <sub>2</sub> ..	37.82'

\* Pyridine Solution.

3. DISCUSSION OF RESULTS

Tables XII and XIII give the difference between the molecular magnetic rotation of different compounds. One notices that the additivity rule is fairly valid. From these tables the ionic rotations have been computed (Table XIV) assuming that the rotation for the hydrogen ion is zero. This is only strictly true if the hydrogen ions in solution consist of free protons. The metal ions have much smaller rotation than the acid ions. Tables XV and XVI give the values of the magneto-optic anomaly for all the solutions for which measurements have been made so far. It must be mentioned here that the  $\gamma$  value for water is 0.76.

It has been reported in a previous paper that the  $\gamma$  values of free ions having the inert gas configuration is very nearly unity and that any deviation of the electron atmospheres from the inert gas state is immediately indicated by the decrease of the anomaly. In the case of ions with strong covalent linkages the electron atmosphere would have considerably departed from the inert gas state and consequently on the basis of the above observation the  $\gamma$  value in such ions should be extremely low. This is found to be so in the

TABLE XII  
*Molecular Rotation*  
(In minutes  $\times$  10)

	H	Li	Na	K	NH <sub>4</sub>	Ca	Sr	Mg	Zn	Cd
Cl-F ..	..	..	12.30	12.20	12.00	..	..	..	..	..
Br-Cl ..	11.49	11.42	11.27	11.36	11.52	11.16	11.20	10.50	10.91	10.8
I-Cl ..	36.79	37.90	38.54	39.51	39.45	..	..	..	..	..

TABLE XIII  
*Molecular Rotation*  
(In minutes  $\times$  10)

	Cl	Br	I	NO <sub>3</sub>	OH	ClO <sub>3</sub>	$\frac{1}{2}$ SO <sub>4</sub>
Li-H ..	0.59	0.42	1.60	0.75	(2.72)	1.01	0.80
Na-Li ..	1.40	1.30	2.04	0.85	1.15	0.43	0.83
K-Li ..	2.35	2.29	3.96	1.95	2.02	..	1.91
NH <sub>4</sub> -Li ..	3.62	3.72	5.23	3.45	3.10	..	3.47

TABLE XIV

*Ionic Rotations*(In minutes  $\times 10$ )

H .. —	Ca .. 1.35	F .. 0.60	ClO <sub>3</sub> .. 7.92	NO <sub>3</sub> .. 2.10
Li .. 0.60	Sr .. 2.38	Cl .. 12.41	BrO <sub>3</sub> .. 15.46	SO <sub>4</sub> .. 2.90
Na ... 1.72	Ba .. 5.88	Br .. 24.10	IO <sub>3</sub> .. 29.75	OH .. .90
K .. 2.70	Mg .. ε	I .. 49.40		
Rb .. 4.09	Zn .. 2.80			
Cs .. 7.21	Cd .. 6.84			
NH <sub>4</sub> .. 4.15	Hg .. 12.66			

case of nitrates, sulphates, chlorates, bromates and iodates (Tables XV and XVI). Further it must be remembered that each of these substances contains at least one metal ion for which  $\gamma = 1$ . The value of the anomaly for the acid radicals (in NO<sub>3</sub>, SO<sub>4</sub>, ClO<sub>3</sub>, BrO<sub>3</sub>, IO<sub>3</sub>) must therefore be considerably lower than the values given in Tables XV and XVI. These figures seem to lend very good support to the idea that the presence of covalent bond decreases the value of  $\gamma$  of a substance. If this were true then the anomaly should be lowest in the groups that contain the strongest covalent bonds.

TABLE XV

*Magneto-optic anomaly of 4 Normal solutions*

	H	Li	Na	K	NH <sub>4</sub>
Cl ..	77.8	79.6	81.4	81.1	79.6
Br ..	79.5	81.1	84.3	83.1	83.4
I ..	79.8	82.9	83.4	85.1	84.7
NO <sub>3</sub> ..	53.3	58.6	59.2	58.0	60.0
½ SO <sub>4</sub> * ..	69.2	71.3	71.6	69.2	69.3
OH ..	76.0	77.0	77.0	76.8	76.3
ClO <sub>3</sub> ..	68.4	72.0	73.6	..	..
BrO <sub>3</sub> ..	67.0	..	73.3	..	..
IO <sub>3</sub> ..	75.5	75.5	..	..	..

\* 2 Molar solution.

TABLE XVI

100 $\gamma$  (4 Molar solutions)

	Ca	Sr	Ba	Mg	Zn	Cd
Cl <sub>2</sub> ..	85.9	76.8	79.4	78.0	75.7	77.4
Br <sub>2</sub> ..	75.2	76.2	..	74.4	77.0	77.9
I <sub>2</sub> ..	..	..	..	..	67.8	68.3
(NO <sub>3</sub> ) <sub>2</sub> ..	43.0	43.3	65.1	43.2	44.4	48.7

An idea of the strengths of these bonds can be obtained from certain Raman frequencies of these groups. Table XVII gives the Raman frequency (Hertzberg, 1946) and the force constants as also the values of the anomaly for 4 Normal solutions of salts containing these ions. One notices that the ions that have the greatest frequency, *i.e.*, the strongest binding have the least value of  $\gamma$  when dissolved in water.

TABLE XVII

Ion	100 $\gamma$ of 4 normal solution	Raman frequency cm. <sup>-1</sup>	Force const. $k \times 10^5$ dynes /cm.
NO <sub>3</sub> ..	58	1050	10.39
SO <sub>4</sub> ..	64	981	9.07
ClO <sub>3</sub> ..	73	930	5.55
BrO <sub>3</sub> ..	74	806	5.25
IO <sub>3</sub> ..	75	779	5.35

The anomaly for pure acids are given in Table XVIII. The low values are most probably due to the covalent linkages that exist in these acids in the pure state. The solutions of the acids in water have a much higher value of the anomaly.

TABLE XVIII

Acid	100 $\gamma$
HNO <sub>3</sub> ..	20.0
H <sub>2</sub> SO <sub>4</sub> ..	42.4
HBr ..	38.0
HCl ..	62.0



The divalent halides of Zn and Cd which are known not to dissociate completely in water have low values of the anomaly. The ammonium salt solutions have a lower value of  $\gamma$  than the corresponding alkali salt solutions probably due to the covalent N-H bond.

#### 4. MAGNETO-OPTIC ANOMALY IN GASES AND VAPOURS

The studies in ionic solutions indicate that there is a relationship between the strength of binding and the magneto-optic anomaly of a molecule. It was therefore thought worthwhile to collect together the values of the anomaly of gases and vapours and to find whether there is any similar relationship there also. Darwin and Watson (1928) have calculated the anomaly in the case of only five gases  $O_2$ ,  $H_2$ ,  $N_2$ ,  $CO_2$  and  $N_2O$ . In the case of other gases and vapours there are measurements of the Faraday effect for one or two wavelengths in the visible region (Landolt & Bornstein Tables). The dispersions of the gases were also obtained from the same source and the values of the anomaly have been calculated. Table XIX gives the value of  $\gamma$  of the different gases and vapours.

TABLE XIX

Gas	Neon	Argon	$H_2$	HCl	$H_2S$	IIBr	$H_2O$
$100\gamma$	116.5	100	99	92.8	89.8	80.8	78
Gas	$SO_2$	$Cl_2$	CO	$N_2$	$CO_2$	$(CN)_2$	$(N_2O)$
$100\gamma$	72.5	70.7	65.6	63.0	53.7	48.1	32.0
Gas	$C_2H_2$	$C_2H_4$	$C_2H_6$	$C_3H_8$	$CH_3Cl$		
$100\gamma$	66.7	61.2	60.1	58.0	48.3		
Gas	$CHCl_3$	$C_2H_5Br$	$CCl_4$	$CS_2$			
$100\gamma$	70.1	77.4	60.4	36.0			

The anomaly in most gases and vapours range from 0.32 to 1.00. The high value of 1.16 in the case of neon is probably due to experimental errors. The  $\gamma$  value of argon is almost exactly the theoretical value of unity. The lower value of the constant found in the other gases must obviously be due to the failure of Larmor's theorem in molecules. Unfortunately the determination of the ratio of the angular momentum of an electron to its magnetic moment in a molecule is a very complicated process and has been accomplished and that too approximately, in the case of the hydrogen molecule (Van Vleck, 1932). It would be of some interest to find out whether there is any relation-

ship between the magneto-optic anomaly and the valence force constant of a molecule. The values of the force constant can be calculated directly from data on Raman and infra-red spectra. Table XX gives the values of  $\gamma$  and the force constants for all the gases for which data are available.

TABLE XX

Gas		Force constant $\times 10^9$ dynes/cm.	$100\gamma$
(CN) <sub>2</sub>	..	17.73	48.2
CO <sub>2</sub>	..	16.8	54
CO	..	11.82	65
SO <sub>2</sub>	..	9.97	72
H <sub>2</sub> O	..	7.76	78
HBr	..	4.00	81
H <sub>2</sub> S	..	4.14	90
HCl	..	5.15	93
H <sub>2</sub>	..	4.99	99
CS <sub>2</sub>	..	8.1	36
CCl <sub>4</sub>	..	4.38	60

From Table XX one can see that the anomaly is very intimately connected with the strength of binding, stronger the binding, the lower is the anomaly. (There are of course many discrepancies, *e.g.*, HBr, CS<sub>2</sub>, CCl<sub>4</sub>, etc.) On this basis it is possible to understand why the value of CH<sub>3</sub>Cl ( $\gamma = 0.48$ ) is lower than that for CHCl<sub>3</sub> ( $\gamma = 0.70$ ). The stretching force constant for  $\text{--C--H}$  is  $4.79 \times 10^9$  dynes/cm. while that for  $\text{C--Cl}$  is only  $3.64 \times 10^9$  dynes/cm. and the latter compound contains more C-Cl bonds than the former. But on this basis it is impossible to explain the intermediate value of  $\gamma = 0.60$  for CCl<sub>4</sub>. The extremely low value of 0.36 for CS<sub>2</sub> does not also find an explanation on this basis.

The author wishes to record his grateful thanks to Prof. R. S. Krishnan for his kind encouragement during these investigations.

#### SUMMARY

The paper records the magneto-optic rotation and the dispersion for a large number of ionic solutions. From these data the magneto-optic anomaly for these solutions have been evaluated. The ionic rotation for the different substances have also been estimated. Amongst the substances studied are halides, nitrates, sulphates, hydroxides, chlorates, bromates and iodates of monovalent and divalent elements. The anomaly in some pure acids have also been determined. The magneto-optic anomaly for about twenty-three gases and vapours have been calculated from the data given in Landolt and Bornstein's tables. It is found that the presence of

ions with covalent linkages decreases the value of the anomaly for water, the decrease being greater if the strength of the covalent bond is greater. In the case of gases also the value of the anomaly is lower for gases in which the strength of the bonds is greater. There are some vapours that do not follow this rule.

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