

THE MAGNETO-OPTIC ANOMALY OF ELECTROLYTES IN AQUEOUS SOLUTION

I. Alkali Halides

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I. INTRODUCTION

RECENT measurements by the author (1947, 1948) of the Faraday rotation in cubic crystals for wave-lengths in the visible region have shown that the Verdet constant of most cubic crystals could well be expressed by the modified Becquerel formula (Darwin and Watson, 1927)

$$V = \gamma \frac{e}{2mc^2} \lambda \frac{dn}{d\lambda}$$

where $dn/d\lambda$ is the dispersion of the substance and γ is a constant called the magneto-optic anomaly. These studies have indicated that the magneto-optic anomaly is very intimately connected with the nature of the binding between atoms or ions. A determination of the magneto-optic anomaly in electrolytic solutions, where the ions are comparatively free, would therefore be invaluable in the understanding of the results obtained with crystals.

Very little systematic work has been done so far on the Faraday rotation of ionic solutions. Moreover, all the investigators on this subject [Jahn (1891), Anderson and Asmussen (1932), Okazaki (1934) and de Mallemann (1942)] have only measured the magnetic rotation of solutions and not their dispersions and as such no data for the magneto-optic anomaly for solutions are available. It was with a view of filling up this gap in the literature that this series of investigations was undertaken by the author. Further, it has been shown from theoretical considerations (Rosenfeld, 1930) that the value of γ for atoms having the inert gas structure is unity. It is therefore of some interest to find out how far this is true in the case of alkali metal ions and halogen ions which have the inert gas configuration.

This paper reports the measurement of the Faraday rotation and the dispersion of seventeen univalent halide solutions and from these the magneto-optic anomaly of the solutions have been evaluated. The rotations and values of γ for the free ions have also been estimated. It is found that the magneto-optic anomaly of ions having the inert gas configuration is very nearly the theoretical value of one.

2. EXPERIMENTAL METHODS

The apparatus that was used in these experiments has already been described (Ramaseshan, 1946; 1947). The source of light was an intense mercury arc with a Zeiss filter for separating out the λ 5461 radiation. The light after passing through a double field polariser went through a longitudinal hole in the pole pieces of a Rutherford magnet and was received by an analyser. The analyser could measure rotations upto 0.01° .

The solutions to be studied were placed in between the two pole pieces. Two identical cells with glass end pieces of the same thickness were made. When both the cells were filled with pure water their magnetic rotations in the same field did not vary by more than 1 in 2,000. One of the cells was filled with pure double distilled water and the other with the solution. By a simple sliding arrangement the two cells could be brought between the pole pieces alternately, the two occupying exactly the same position. This arrangement removes any errors that may arise due to the non-uniformity of the field. For any current flowing through the magnet the rotations for the water and the solution were consecutively measured. This avoids errors due to fluctuations in the mains voltage. The measurements were made at room temperature which was about 25°C .

The solutions were prepared from Kahlbaum's or Merck's purest analytical reagents. A 4-molar solution was accurately prepared. The density of the solution was measured with a specific gravity bottle.

The refractive indices of the solutions were measured for λ 5893 (Na), λ 5461 (Hg) and λ 4358 (Hg) by means of Pulfrich refractometer. A special water circulating arrangement kept the temperature constant during the course of the measurement. The values of the refractive index are accurate to one unit in the fourth place of decimals and the values of the dispersions are accurate to two units in the fifth place.

3. METHODS OF CALCULATION AND RESULTS

The specific rotations of the ions in solution are evaluated from the simple Verdet rule (1858)

$$[V_s] = [V_i] x_1 + [V_\omega] x_2,$$

where $[V_s]$, $[V_i]$ and $[V_\omega]$ are the specific rotations of the solution, the ions in solution and water, x_1 and x_2 are the number of grams of salt and water in 100 grams of solution. The specific rotation is defined as $[V] = V/d$, where V is the Verdet constant and d is the density of the substance. The molecular rotation is $[V]_M = MV/d$, where M is the molecular weight of the

substance. The magneto-optic anomaly γ for any solution is calculated from the modified Becquerel formula.

The magnetic rotations of the solutions were measured for $\lambda 5461$ with water as the standard substance. The absolute value of the Verdet constant for $\lambda 5461$ for water has been taken as $0.01547'$ per cm. per oersted at $25^\circ C$. (Rodger and Watson, 1896).

Tables I-VII give the optical and the magneto-optic constants for water and the different alkali halide solutions. In these M is the molecular weight, X_1 and X_2 give the number of grams of salt and water in $100\text{ c.cs. of solution}$, d the density, n the refractive index and $\Delta n = n_{5893} - n_{4358}$, V_{5461} the Verdet constant of the solution, $[V_i]_M$ the molecular rotation of ions in solution calculated from the Verdet mixture rule and γ is the magneto-optic anomaly for the solutions. The value of $\frac{9n}{(n^2+2)^2}$ for each solution has also been included in the tables. These values will be made use of in the calculation of the value of γ for the individual ions.

TABLE I
The optical and magneto-optic constants for water

n_{5893}	n_{5461}	n_{4358}	$\Delta n \times 10^5$	V_{5461}	100γ
1.33239	1.33381	1.33953	714	0.01547	76

TABLE II
*The magneto-optic data for univalent chloride solutions
(4 Normal)*

	M	X_1	X_2	d	$V_{5461} \times 10^3$	$[V_i]_M \times 10$	100γ
HCl	36.46	14.60	92.16	1.0674	19.30'	12.61'	77.8
LiCl	42.40	16.99	92.13	1.0909	19.49'	13.10'	79.6
NaCl	58.46	23.38	91.91	1.1529	20.02'	14.50'	81.4
KCl	74.56	29.86*	87.68	1.1750	19.74'	15.45'	81.1
CSCl	120.94	48.31	85.67	1.3404	19.93'	16.70'	81.5
RbCl	168.37	67.37	83.02	1.5036	20.77'	19.82'	80.8
NH ₄ Cl	53.50	21.42	84.32	1.0572	19.73'	16.72'	79.6

* Super saturated solution.

TABLE III
*The optical data for univalent chlorides in solutions
(4 Normal)*

	n_{5893}	n_{5461}	n_{4358}	$\Delta n \times 10^5$	$\frac{9n}{(n^2+2)^2} \times 10^2$	
HCl	..	1.36401	1.36575	1.37272	871	82.27
LiCl	..	1.36580	1.36752	1.37439	859	82.17
NaCl	..	1.36879	1.37051	1.37742	863	82.00
KCl	..	1.36811	1.36982	1.37666	855	82.04
RbCl	..	1.37194	1.37366	1.37953	859	81.82
CsCl	..	1.38108	1.38282	1.38980	872	81.31
NH ₄ Cl	..	1.37018	1.37192	1.37887	869	81.92

TABLE IV
The magneto-optic data for univalent bromide solutions

	M	X ₁	X ₂	d	$V_{5461} \times 10^3$	$[V_i]_M \times 10$	100γ
HBr	..	80.92	32.4	90.01	1.2238	23.56'	24.10'
LiBr	..	86.85	34.75	89.54	1.2428	23.65'	24.52'
NaBr	..	102.91	41.16	89.43	1.3059	24.56'	25.82'
KBr	..	119.09	47.60	84.72	1.3235	23.83'	26.81'
NH ₄ Br	..	97.95	39.18	82.03	1.2121	23.98'	28.24'

TABLE V
*The optical data for univalent bromide solutions
(4 Normal)*

	n_{5893}	n_{5461}	n_{4358}	$\Delta n \times 10^5$	$\frac{9n}{(n^2+2)^2} \times 10^2$	
HBr	..	1.38192	1.38400	1.39232	1040	81.24
LiBr	..	1.38144	1.38349	1.39167	1023	81.27
NaBr	..	1.38532	1.38737	1.39555	1023	81.05
KBr	..	1.38330	1.38531	1.39337	1007	81.17
NH ₄ Br	..	1.38681	1.38882	1.39689	1008	80.97

TABLE VI
*The magneto-optic data for univalent iodide solutions
 (4 Normal)*

	M	X ₁	X ₂	d	V ₅₄₆₁ × 10 ³	[V _i] _M × 10 ³	100γ
HI	..	127.92	51.16	85.76	1.3692	33.02'	49.40'
LiI	..	133.86	53.54	85.49	1.3903	33.62'	51.00'
NaI	..	149.91	59.96	83.26	1.4322	34.09'	53.04'
KI	..	166.02	66.41	80.78	1.4719	34.48'	54.96'
NH ₄ I	..	144.96	57.98	78.4	1.3692	34.70'	56.23'

TABLE VII
*The optical-data for univalent iodide solutions
 (4 Normal)*

	n ₅₈₉₃	n ₅₄₆₁	n ₄₃₅₈	Δn × 10 ⁵	$\frac{9n}{(n^2+2)^2} \times 10^2$
HI	1.39521	1.39811	1.40973	1452	80.45
LiI	1.41427	1.41711	1.42850	1423	79.54
NaI	1.41684	1.41971	1.43119	1435	79.24
KI	1.41520	1.41804	1.42943	1423	79.33
NH ₄ I	1.41544	1.41831	1.42981	1437	79.31

4. THE MAGNETO-OPTIC ANOMALY OF THE IONS

From the data obtained in the previous section the magneto-optic anomaly of the ions as distinct from that of the solution can be calculated in the following way. The specific rotation of the ions can be calculated from one of the two mixture rules.

$$[V_s] = [V_i] x_1 + [V_w] x_2 - \text{Verdet (1858)}$$

or

$$\frac{9n_s}{(n_s + 2)^2} [V_s] = \frac{9n_i}{(n_i + 2)^2} [V_i] x_1 + \frac{9n_w}{(n_w + 2)^2} [V_w] x_2$$

de Mallemann (1926)

where [V] is the specific rotation, n the refractive index and x₁ and x₂ the weight percentage of the salt and water. The subscripts s, i and w stand

for the solution, ions and water. The second formula has been derived from the first on the assumption that the Verdet rule is only true for gaseous mixtures and that in other cases, a correction for the Lorentz field has to be introduced. The correction factor was obtained from the accurate experimental results of de Malleman and Gabiano (1933) who found that

$$[V]_{\text{vapour}} = \frac{9n_i}{(n_i^2 + 2)^2} [V]_{\text{liquid}}.$$

Although experiments have not yet decisively indicated the superiority of either of the mixture rules, the one due to de Malleman is used in the following calculations as it has a greater theoretical justification. It is clear from the above that if the dispersion of the ions can be calculated from the dispersion data for the solutions the value of γ for the ions can be evaluated.

The mixture rule for refraction is given by

$$\frac{n_s^2 - 1}{n_s^2 + 2} \times \frac{1}{d_s} = \frac{n_i^2 - 1}{n_i^2 + 2} \times \frac{1}{d_i} x_1 + \frac{n_\omega^2 - 1}{n_\omega^2 + 2} \times \frac{1}{d_\omega} x_2$$

differentiating this equation we have

$$\frac{9n_s}{(n_s^2 + 2)^2} \frac{dn_s}{d\lambda} \times \frac{1}{d_s} = \frac{9n_i}{(n_i^2 + 2)^2} \frac{dn_i}{d\lambda} \times \frac{1}{d_i} x_1 + \frac{9n_\omega}{(n_\omega^2 + 2)^2} \frac{dn_\omega}{d\lambda} \times \frac{1}{d_\omega} x_2$$

The dispersion of the ions can be directly calculated from this formula. If we put

$$\frac{n^2 - 1}{n^2 + 2} \times \frac{1}{d} = [R] \text{ the refractivity.}$$

$$\frac{9n}{(n^2 + 2)^2} \times \frac{1}{d} \frac{dn}{d\lambda} = [D] \text{ the dispersivity}$$

and

$$\frac{9n}{(n^2 + 2)^2} [V] = [\Omega] \text{ the rotativity.}$$

Then the mixture rules can be written as

$$[R_s] = [R_i] x_1 + [R_\omega] x_2 \quad \text{refraction}$$

$$[D_s] = [D_i] x_1 + [D_\omega] x_2 \quad \text{dispersion}$$

$$[\Omega_s] = [\Omega_i] x_1 + [\Omega_\omega] x_2 \quad \text{rotation (de Mallemann)}$$

$$[V_s] = [V_i] x_1 + [V_\omega] x_2 \quad \text{rotation (Verdet)}$$

Since

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

$$\gamma_{\text{ion}} = \frac{[\Omega_i]}{\frac{e}{2mc^2} \lambda [D_i]}$$

The formulæ given above make the following assumptions (a) the Lorentz-Lorenz formula for refraction is true in ionic assemblies and (b) the optical and magneto-optical properties of water do not change due to the presence of the ions in solution. It is also quite obvious that the value of γ obtained by this method gives only the anomaly of the hydrated or solvated ion.

Table VIII gives value of γ_{ion} for the 17 halides calculated from the data given in Tables II to VII. The table also gives the value of the Molecular Dispersivity $[D_i]_M = M [D_i]$ the molecular rotativity $[\Omega_i]_M$ and the molecular rotation $[V_i]_M$ of the alkali halides ion in solution. The errors in the values of $[D_i]_M$, $[\Omega_i]_M$, $[V_i]_M$ and γ_{ion} would be of the order of 3 to 4 per cent.

TABLE VIII

		$[D_i]_M$	$[V_i]_M$	$[\Omega_i]_M$	$100\gamma(\text{ions})$
HCl	..	11.57	12.61	9.73	84
LiCl	..	10.76	13.10	10.01	93
NaCl	..	11.33	14.50	11.14	98
KCl	..	12.46	15.45	12.00	96
RbCl	..	13.38	16.70	12.89	96
CSCl	..	15.10	19.82	15.24	101
NH ₄ Cl	..	14.55	16.72	12.94	89
HBr	..	21.64	24.10	18.59	86
LiBr	..	20.89	24.52	18.95	91
NaBr	..	20.75	25.82	20.67	99
KBr	..	21.88	26.81	20.80	95
NH ₄ Br	..	22.22	28.24	19.82	86
HI	..	50.7	49.40	38.5	76
LiI	..	43.7	51.00	39.0	90
NaI	..	45.0	53.04	40.5	91
KI	..	45.8	54.96	42.0	91
NH ₄ I	..	47.2	56.23	43.2	91

5. DISCUSSION OF RESULTS

From the scrutiny of the tables, one notices that while the contribution of the anion to the magnetic rotation is considerable, that due to the cation is comparatively small. Further the variation in rotation produced by a change in the acid radical is much more pronounced than that produced by a change in the metallic radical. Table IX gives the differences of the values of $[V_i]_M$ for the compounds. From these the molecular magnetic rotation of individual ions may be computed if the value for one of the ions is arbitrarily fixed. As an approximation, it may be assumed that the rotation due to the hydrogen ion is zero. On this basis the average ionic rotations have been computed and given in Table X. Since the values for the cations are small they are less accurate than those for the anions,

If the ionic rotations are plotted against the atomic number, curves very similar to those obtained by Fajans and his collaborators (1924) for ionic volumes and ionic refractivities are obtained. One can see that the additivity rule is only approximately valid. This is probably because the solutions are too concentrated. But unfortunately in the case of dilute solutions the rule cannot be tested as large errors enter in the measurement of the dispersion and Faraday rotation.

TABLE IX
Molecular rotation in mins. $\times 10$

	H	Li	Na	K	NH ₄
Cl—F	12.30	12.20	12.00
Br—Cl	..	11.49	11.42	11.27	11.52
I—Cl	..	36.79	37.90	38.54	39.46

	Cl	Br	I
Li—H	0.59	0.42	1.60
Na—Li	1.40	1.30	2.04
K—Li	2.35	2.29	3.96
NH ₄ —Li	3.62	3.72	5.23

TABLE X
Ionic rotations in mins. $\times 10$

H	Li	Na	K	Rb	CS	NH ₄	Cl	Br	I
ϵ	0.60	1.72	2.70	4.09	7.21	4.15	12.41	24.10	49.40

Table XI give the γ values for the different halide solutions. The value of γ for water is 0.76. One notices that the presence of the halides of alkali metals in water increases its γ value. This obviously means that the γ value of the ions is higher than that of water, a fact which finds proof from the figures in Table VIII. The experiments of the author on crystals (*loc. cit.*) indicate that the presence of covalent linkages tend to reduce the value of γ . If this were true the lower values of γ of HCl, HBr and HI than those for the corresponding halides of the alkali metals may either be due to the acids

not being completely dissociated or due to the formation of other types of groups by the free hydrogen ions. The values of the anomaly for the pure acids HCl and HBr are respectively 62% and 38%. The low values are most probably due to the covalent linkages that are known to be present in these acids in the pure state. In solutions, however, the values of γ are higher than those for the pure acids because of the ionisation.

TABLE XI
The magneto-optic anomaly of 4 normal solution
100 γ

	H	Li	Na	K	NH ₄
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

As already pointed out Rosenfeld has shown that for gases having the inert gas configuration the value of γ is unity. The author has calculated the values of γ for argon and neon from the optical and magneto-optic data given in Landolt and Bornstein Tables. The values of the Verdet constant and the value of the anomaly for these gases are given in Table XII.

TABLE XII
The magneto-optic anomaly in rare gases

Gas	$V_{5461} \times \frac{10^{-6} \text{ min.}}{\text{per cm. per oersted}}$	100 γ
Neon ..	1.1	116.5
Argon ..	9.2	100.6

One notices that the values of γ for these gases are 1.16 and 1.00. Neon has an exceedingly small Verdet constant of 1.1×10^{-6} minutes per cm. per oersted; only a sixth of the value found in hydrogen gas. Since no other substance has been found to have a γ value of more than 1, it is quite probable that this high value of γ in neon is due to experimental errors.

Since free ions of the alkali metals and the halogens have the inert gas configuration they too should obey the Becquerel formula, *i.e.*, $\gamma = 1$. Table VIII shows that γ value of the ions in solution varies from 0.90 to 1.00. It must be remembered that in the calculation of the anomaly for the ions

many assumptions have been made, for instance the validity of the Lorentz-Lorenz formula for refraction in ionic assemblies. Further the values of γ found are those for solvated or hydrated ions and the energy of solvation as found from absorption spectra data (Gurney, 1936) is quite considerable. Nevertheless these experiments and calculations show that *in inert gases and in ions having the inert gas configuration the Faraday effect very nearly obeys the unmodified Becquerel formula (i.e., $\gamma = 1.00$).*

Fajans and Joos (1924) have found that the molecular refractivity of ions in solution is much larger than the value for the same ions in the crystalline state. This difference in the refractivity they attribute to the distortion of the electron atmospheres by the crystalline fields. Table XIII gives a collection of the data of molecular refractivity dispersivity, magnetic rotativity magnetic rotation and the magneto-optic anomaly for ions in solution and the crystalline state for the four substances NaCl, KCl, KBr and KI.

TABLE XIII
Refractive and magneto-optic constants of crystals and their solutions

Substance	[R _i] _M		[D _i] _M		[Ω _i] _M		[V _i] _M		100γ ion		
	Cry.	Soln.	Cry.	Soln.	Cry.	Soln.	Cry.	Soln.	Cry.	Soln.	
NaCl	..	8.57	9.469	8.18	11.33	8.09	11.14	11.08	14.50	90	98
KCl	..	10.90	11.43	10.22	12.46	9.23	12.00	12.29	15.45	82	96
KBr	..	14.05	15.05	18.38	21.88	15.41	20.80	21.63	26.81	79	95
KI	..	19.92	21.76	35.90	45.80	28.74	42.00	44.01	54.96	79	91

It is clear from the table that in every case the value of the constant for the ions in solution is much greater than that for the ions in the crystalline state. One notices also that these differences are largest in the case of the magnetic rotation and rotativity. These figures seem to indicate that Faraday effect can be used as a sensitive tool for the determination of any distortions in the electron atmospheres in atoms or ions.

In conclusion, the author wishes to thank Prof. R. S. Krishnan for the kind interest he took in these investigations.

SUMMARY

The Verdet constant and dispersions of 4-normal solutions of seventeen univalent halides have been measured. From these, the values of the magneto-optic anomaly have been estimated. The magneto-optic anomaly of the

free ions of the alkali halides as distinct from that of the solution have been evaluated. It is found that the value of the anomaly of the free ions having the inert gas configuration is very near the theoretical value of 1. The ionic dispersivity and rotativity of the individual ions have been estimated. It is found that the additivity rule is approximately valid. The pure acids, HCl, HBr and HI, have values of the anomaly much lower than those for their solutions. This has been attributed to the presence of covalent linkages in the acids in the pure state. The anomaly for the rare gases neon and argon are very nearly unity. It is found that the values of molecular refractivity, dispersion, rotativity, rotation and the magneto-optic anomaly of the ions in solution are higher than those for the ions in the crystalline state.

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