MAGNETO-OPTIC CONSTANTS OF IONS IN AQUEOUS SOLUTIONS

By V. Sivaramakrishnan

(Department of Physics, Indian Institute of Science, Bangalore-3)

Received February 23, 1957

Abstract

The magneto-optic rotation for λ 5461 Å and the optical dispersion have been measured for some acids and their salts at various concentrations and from these data the specific Verdet constant, the molecular magnetic rotativity, optical dispersivity and the magneto-optic anomaly factor have been estimated. It is found that all these constants vary considerably with concentration thereby revealing that the intrinsic magneto-optic polarisability of the ions varies with concentration. Therefore the values, extrapolated to infinite dilution have also been determined and from these the specific Verdet constant and the magnetic rotativity of the different anions and cations have been found out.

1. Introduction

The magnetic rotation of the plane of polarisation of electrolytes in aqueous solutions has been the subject of many experimental studies. Much of our present knowledge of the Faraday rotation of ions in solution is due to the investigations of Anderson and Asmussen (1932), Okazaki (1933, 1935) and De Mallemann (1939, 1942), who have accurately determined the values of magnetic rotations for different ions in solution. The values reported by these authors have been obtained from studies on solutions of fairly high concentrations. It is well known that the ionic rotation varies considerably with concentration. Even from the data presented by the above workers, one notices that the rotations of the ions vary as much as 10 to 15% with concentration. Hence if one wants to compare the magneto-optic properties of different ions, one has to find the ionic rotations at various concentrations and extrapolate it to infinite dilution. It was with a view to fill up this gap in the literature the present investigation was undertaken. Also the molecular magnetic rotativity, optical dispersivity, and the magneto-optic anomaly factor of the substances in aqueous solutions have been determined. The results are presented below.

2. Methods of Calculation

The experimental set-up and the procedure are similar to that described in an earlier publication of the author (1954). The magnetic rotation and the optical dispersion have been measured at large number of concentrations and the calculated

108

values of ionic rotation, rotativity and the dispersivity were extrapolated to infinite dilution. The values of Verdet constant were accurate to 1%. The values of Verdet constant for the halogen acids reported in an earlier publication of the author (1954) were found to be greater than the correct value by 2 to 3% due to a systematic error. An error of 2% in the value of Verdet constant at dilute solutions would introduce an error of more than 5% in the values of ionic rotations and the anomaly factor. Necessary care was taken in the present studies to avoid any such error.

The following simple mixture rules have been employed for the evaluation of the magneto-optic constants of ions in solution from the data for the solution and the solvent.

$$[X]_{sol.} = [X]_1 w_1 + [X]_2 w_2$$

where [X] represents either the specific Verdet constant

$$[V] = \frac{V}{d}$$

or the magnetic rotativity

$$[\Omega] = \frac{9n}{(n^2 + 2)^2} \frac{V}{d},$$

or the molecular dispersivity,

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

w_1 and w_2 are the weight percentage of the solute and the solvent in the solution, V is the Verdet constant and $dn/d\lambda$ the optical dispersion. The subscripts 1, 2 and sol. refer to the solute, the solvent and the solution respectively. The molecular magneto-optic constants are obtained by multiplying the specific Verdet constant, rotativity and dispersivity of the solute by its molecular weight M and are denoted by $[V]_M$, $[\Omega]_M$ and $[D]_M$ respectively. The values of the magneto-optic anomaly factor for the salts in solution are calculated from the relation

$$\gamma_{salt} = \frac{[\Omega]_M}{e/2mc^2 \cdot \lambda [D]_M}$$

All the solutions were prepared from Kahlbaum's or from Merck's pure analytical reagents.

3. RESULTS

Table I gives the magneto-optic data of the acids and salts studied here. Only the results at two representative concentrations from the large number of concentrations at which measurements have been made, are given in this table along with the extrapolated value at the zero concentration. $[V]_M$, $[\Omega]_M$, $[D]_M$ and γ are respectively the molecular specific Verdet constant, molecular rotativity, molecular dispersivity and the magneto-optic anomaly factor of the salts in solutions for the

TABLE I

Magneto-Optic Data of Acids and Salts in Solution

Substance	%	Density	Verdet constant mins./cm./oersted	$[V]_M$ in radians $\times 10^6$	$[\Omega]_M$ in radians $\times 10^6$	$[D_M]$	γ
HCl	..	..	..	401	318	27·0	0·75
	23·34	1·1128	0·02249	377	289	23·9	0·75
	35·5	1·1735	0·02597	353	272	22·7	0·75
HBr	..	..	..	736	588	47·6	0·78
	16·75	1·1269	0·02041	732	572	45·2	0·79
	44·3	1·4294	0·03160	716	538	41·6	0·81
HI	..	..	..	1649	1315	101·9	0·81
	29·9	1·2709	0·03016	1602	1241	93·4	0·83
	46·17	1·5057	0·04198	1575	1178	86·3	0·85
HNO₃	..	..	..	66	40	32·8	0·07
	28·52	1·1659	0·01422	71	42	29·5	0·09
	50·81	1·3073	0·01273	76	51	26·7	0·12
H₂SO₄	..	..	..	146	94	16·6	0·35
	27·2	1·1938	0·01524	156	106	16·5	0·40
	77·0	1·6868	0·01371	169	125	16·6	0·47
HClO₄	..	..	..	79	45	15·6	0·18
	17·0	1·1018	0·01470	85	52	15·1	0·21
	45·9	1·3515	0·01329	92	62	14·5	0·27
H₃PO₄	..	..	..	214	157	20·3	0·48
	24·3	1·1394	0·01552	221	162	19·8	0·51
	61·0	1·4326	0·01561	227	171	18·7	0·57
LiCl	..	..	..	407	314	22·2	0·88
	7·8	1·0414	0·01750	400	310	21·9	0·88
	18·0	1·1010	0·02029	393	302	21·5	0·88
NaCl	..	..	..	493	407	25·9	0·98
	9·4	1·0640	0·01776	477	373	25·0	0·93
	18·0	1·1289	0·01961	442	341	24·3	0·88
KCl	..	..	..	525	419	27·1	0·97
	9·5	1·0584	0·01719	505	396	26·0	0·93
	17·84	1·1153	0·01862	480	376	25·7	0·88
NH₄Cl	..	..	..	545	427	32·3	0·83
	9·74	1·0268	0·01779	532	417	30·4	0·85
	19·0	1·0519	0·01984	516	402	29·3	0·85
NaBr	..	..	..	824	646	44·6	0·91
	13·7	1·1117	0·01904	811	627	43·1	0·91
	36·4	1·3615	0·02558	736	563	40·2	0·87
KBr	..	..	..	848	683	46·6	0·91
	9·44	1·0675	0·01743	840	663	45·8	0·90
	32·15	1·2796	0·02258	768	610	44·3	0·87

TABLE I—(*Contd.*)

| Substance	%	Density	Verdet constant mins./cm./oersted	$[V]_M$ in radians $\times 10^6$	$[\Omega]_M$ in radians $\times 10^6$	$[D_M]$	γ
NH_4Br ..	9·5	1·0533	0·01785	880	699	51·6	0·85
	33·0	1·2126	0·02475	874	690	50·8	0·85
				866	670	49·0	0·85
KI ..	17·6	1·1405	0·02165	1754	1404	96·5	0·91
	50·4	1·5480	0·03822	1708	1357	93·9	0·90
				1630	1239	92·2	0·85
NH_4I ..	9·45	1·0596	0·01895	1788	1416	103·5	0·85
	53·9	1·4838	0·04194	1784	1357	100·9	0·85
				1652	1239	96·1	0·81
$CaCl_2$ ..	10·3	1·0845	0·01795	850	647	45·4	0·89
	30·8	1·2882	0·02357	831	626	44·5	0·88
				794	580	43·5	0·84
$SrCl_2$ ..	8·43	1·0757	0·01692	890	651	42·2	0·96
	17·8	1·1753	0·01866	841	623	39·1	0·96
				812	602	39·7	0·95
$BaCl_2$ ..	5·25	1·0446	0·01626	1030	777	47·7	1·02
	17·24	1·1701	0·01824	1014	757	45·6	1·02
				970	724	44·7	1·03

wavelength λ 5461 Å. In Table II are given the calculated values of ionic rotations and rotativity for λ 5461 Å from the extrapolated results. The ionic rotations and rotativity of the anions were determined on the assumption that the rotation due to the hydrogen-ion is zero. From these values the constants for the cations were evaluated. The values given in the table for the cations are the mean of many values got from different halogen salts.

It is worthwhile to remark here that at the same higher concentrations, the values of magnetic rotations of the substances in solution determined now by the author agrees fairly well with those of other workers (Anderson and Asmussen, 1932; Okazaki, 1933; De Mallemann, 1941). But it can be seen from the tables that the values of $[V]_M$, $[\Omega]_M$ and $[D]_M$ of the ions vary considerably with concentration. Since the values of magnetic rotation and rotativity increases by about 10% with decrease in concentration, the estimated values of ionic rotation and rotativity in the present studies are greater than those of other observers who have obtained them from their results at higher concentration. The values of specific Verdet constant and rotations of the anions given in Table II are accurate to 2 to 3% only and the values of these constants for the cations are very uncertain. This can be easily understood when one remembers that the values of rotativity of the salt itself (both anion and cation together) is accurate to 2% only. This explains the disparity in the values of ionic rotations for cations reported by various workers.

TABLE II

Molecular Rotation and Rotativity of the Ions

Anions	Specific Verdet constant in radians $\times 10^6$	Rotativity in radians $\times 10^6$	Cations	Specific Verdet constant in radians $\times 10^6$	Rotativity in radians $\times 10^6$
Cl^-	401	318	Li^+	6	-4
Br^-	736	588	Na^+	90	75
I^-	1649	1315	K^+	114	96
NO_3^-	67	40	NH_4^+	142	107
ClO_4^-	79	45	Ca^{++}	48	11
SO_4^{--}	146	94	Sr^{++}	88	15
PO_4^{---}	214	157	Ba^{++}	228	141

From a study of Table II, one can get the following series of inequalities for the ionic rotation and rotativity just as in ionic refractivity.

$$Cl^- < Br^- < I^-; \quad NO_3^- < ClO_4^- < SO_4^{--} < PO_4^{---}$$
$$Li^+ < Na^+ < K^+ < NH_4^+; \quad Ca^{++} < Sr^{++} < Ba^{++}.$$
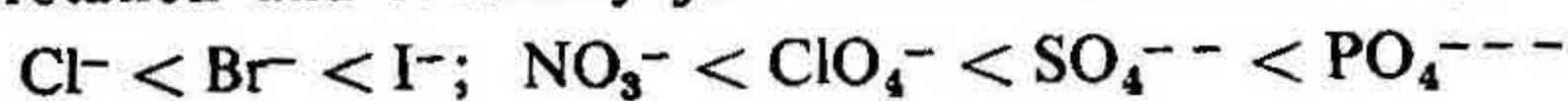
Another important fact that can be noticed from Table I is that whether one uses the simple Verdet rule or the rotativity rule due to De Mallemann

$$\left\{ \frac{9n}{(n^2 + 2)^2} \frac{V}{d} \right\}$$

on the assumption that the Lorentz Lorenz polarisation field exists in ionic assemblies, or the rotativity rule (nV/d) derived from the Drude form of equation, the variation of ionic rotativity with concentration is quite considerable thereby clearly indicating that the intrinsic magneto-optic polarisability of the ions in solution varies with the concentration. This could be probably due to the presence of undissociated molecules or formation of complexes in solution or the hydration of ions due to water molecules.

REFERENCES

1. Anderson and Asmussen   ..   *J. Phys. Chem.*, 1932, **36**, 2819.
2. Mallemann, De   ..   *Ann. de Phys.*, 1942, **17**, 360.
3. Mallemann and Guillaume..   *C.R.*, 1939, 208, 436.
4. Okazaki   ..   *Mem. Ryojum. Col. Eng.*, 1933, **6**, 181; 1935, **8**, 1.
5. Sivaramakrishnan   ..   *Proc. Ind. Acad. Sci.*, 1954, **39**, 31.