

MAGNETO-OPTIC STUDY OF SOME INORGANIC ACIDS AND THEIR SALTS

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Measurements have been made of the optical and magneto-optic constants of aqueous solutions of HNO_3 , H_2SO_4 , HClO_4 and H_3PO_4 and some of their salts at different concentrations. From the observed data the constants for the ions in solution have been evaluated. It is found that while the dispersion in the acids increases, the Verdet constant decreases with concentration. This effect has been attributed to the presence of near U.V. bands which contribute towards dispersion but not towards Faraday rotation. The magneto-optic anomaly factor for these acids is very low; $\gamma(\text{HNO}_3) = 0.2$, $\gamma(\text{HClO}_4) = 0.38$, $\gamma(\text{H}_2\text{SO}_4) = 0.53$, $\gamma(\text{H}_3\text{PO}_4) = 0.62$. and the γ value for the ions changes considerably with concentration.

1. INTRODUCTION

Recent measurements of the optical and magneto-optical constants of aqueous solutions of some halogen acids and their salts have shown that the decrease of the magneto-optic anomaly factor from unity is a measure of the deviation of the ions from their ideal inert gas structures (Sivaramakrishnan, 1954; Ramaseshan, 1950). It was therefore considered that a measurement of the magneto-optic constants of aqueous solutions of acids and salts with ions containing strong covalent bonds would be of some interest. In this paper are reported the results obtained from measurements of magneto-optic constants of solutions of HNO_3 , H_2SO_4 , HClO_4 , H_3PO_4 and of their corresponding salts at different concentrations.

2. DETAILS OF THE EXPERIMENT AND CALCULATION

The magnetic rotations of the different solutions were measured for $\lambda 5461 \text{ \AA}$ by using a Rutherford type of magnet. The refractive indices at different wavelengths were measured using a Pulfrich refractometer provided with an arrangement for maintaining the temperature constant. The details of the experimental set-up used and also the method of calculation have already been reported in a previous paper by the author on halogen acids (Sivaramakrishnan, 1954).

The following simple rules have been used for the evaluation of the constants of the ions in solution from the data for the solution and the solvent.

$$[X]_s F_s = [X_1] F_1 + [X_2] F_2 \quad (1)$$

where $[X]$ represents molecular rotativity $\frac{9nV}{(n^2 + 2)^2} \frac{M}{d}$, or molecular dispersivity $\frac{9n}{(n^2 + 2)^2} \frac{dn}{d\lambda} \frac{M}{d}$, or molecular refractivity $\frac{n^2 - 1}{n^2 + 2} \frac{M}{d}$. F is the mole fraction, d the density, V is the Verdet constant and $dn/d\lambda$ the optical dispersion. The subscripts 1, 2 and s refer respectively to the solute, the solvent and the solution.

Using the modified Becquerel formula

$$V = \gamma \frac{e}{2mc^2} \lambda \left(\frac{dn}{d\lambda} \right)_\lambda \quad (2)$$

the anomaly factor γ for the ion is calculated from the formula

$$\gamma_{\text{ion}} = \frac{[\Omega_i]_M}{\frac{e}{2mc^2} \cdot \lambda [D_i]_M} \quad (3)$$

The solutions were prepared by using Kahlbaum's purest analytical reagents and the acids were further distilled in the laboratory.

3. RESULTS

Since the contribution made by the cation towards the total rotation and dispersion is very small, it has not been possible to separate accurately the different contributions made by the cation and anion. Hence the values given in the tables are for both the ions together. Tables I and II give the optical and magneto-optic data for the acid solutions and salt solutions respectively. Here W is the weight % of the solute, n_{5461} the refractive index for λ 5461, $(dn/d\lambda)_{5461}$ the optical dispersion, $[\Omega_i]_M$, $[D_i]_M$ and $[R_i]_M$ are the molecular rotativity, dispersivity and refractivity of the ions (cation and anion together) and γ_i the anomaly factor of the ions. Figs. 1 to 4 show the variation of the Verdet constant and dispersion with concentration for the different acids. Table III presents the γ values for the pure acids at 100% concentration. These values were obtained by two methods:—the first by using the mixture rule and extrapolating from the values of γ for various concentrations and the other by taking the extrapolated value for the Verdet constant and the dispersion at 100% concentration. The two

TABLE I. Optical and magneto-optic constants of the inorganic acids

Substance	W % acid	Density	V _{sol.} min./cm. per oersted	n ₅₄₆₁	($\frac{dn}{d\lambda}$) ₅₄₆₁ per Å	[Ω_i] _M min./cm. per oersted	[D _i] _M per Å	[R _i] _M	γ_i
HNO ₃	0	1.02	32.82	10.78	.06
	15.58	1.0852	.01480	1.35533	442.5	1.207	31.17	10.67	.07
	28.52	1.1659	.01414	1.37387	505.1	1.339	29.54	10.60	.08
	40.39	1.2430	.01335	1.38866	561.1	1.439	28.27	10.43	.09
	50.81	1.3073	.01256	1.39799	597.1	1.631	26.70	10.28	.11
	62	1.3676	.01161	1.40269	609.8	1.882	24.40	10.13	.14
HClO ₄	0	1.52	15.56	..	.18
	9.1	1.0501	.01506	1.33993	368.3	1.659	15.33	12.78	.20
	17	1.1018	.01471	1.34567	371.2	1.824	15.09	12.69	.22
	19.1	1.1165	.01462	1.34769	372.3	1.862	15.11	12.67	.22
	35.25	1.2448	.01385	1.36249	379.1	2.078	14.81	12.68	.25
	45.88	1.3515	.01332	1.37613	384.6	2.173	14.44	12.68	.27
60	1.5261	.01253	1.39828	399.0	2.324	14.60	12.65	.29	
H ₂ SO ₄	0	3.27	16.59	13.77	.36
	27.23	1.1938	.01524	1.36776	393.3	3.626	16.52	13.73	.40
	46.72	1.3598	.01482	1.39207	409.7	3.896	16.49	13.64	.43
	62.55	1.5217	.01435	1.41412	421.6	4.104	16.40	13.61	.45
	77	1.6868	.01365	1.43266	432.4	4.270	16.56	13.54	.47
	92	1.8121	.01250	1.43163	418.4	4.669	16.69	13.49	.51
H ₃ PO ₄	0	5.41	20.26	14.87	.48
	12.26	1.0646	.01549	1.3459	376.9	5.507	20.11	14.80	.50
	24.29	1.1394	.01552	1.35818	388.7	5.579	19.83	14.71	.51
	37	1.2289	.01556	1.37225	402.7	5.708	19.63	14.50	.53
	53.94	1.3667	.01558	1.39315	415.1	5.809	18.79	14.43	.56
	61	1.4326	.01561	1.40266	421.8	5.869	18.66	14.39	.57
	87.4	1.7128	.01567	1.43979	448.6	6.172	18.60	14.32	.60
100	1.866	.01571	1.45805	459.4	6.362	18.60	14.32	.62	

TABLE II. Optical and magneto-optic constants of the salts

Substance	W % acid	Density	V _{sol.} min./cm. per oersted	n ₅₄₆₁	($\frac{dn}{d\lambda}$) ₅₄₆₁ per Å	[Ω_i] _M min./cm. per oersted	[D _i] _M per Å	[R _i] _M	γ_i
NaNO ₃	32.32	1.2407	.01495	1.37068	486.8	2.77	29.57	11.29	0.17
KNO ₃	25.56	1.1733	.01496	1.35809	439.8	3.29	31.48	13.07	0.19
NH ₄ NO ₃	34.85	1.1476	.01483	1.37913	507.7	4.678	36.04	15.30	0.23
Na ₂ SO ₄	24.39	1.2349	.01611	1.36892	396.0	4.95	17.12	15.31	0.52
(NH ₄) ₂ SO ₄	33.58	1.1909	.01634	1.38559	417.9	9.74	31.21	23.47	0.56
NH ₄ ClO ₄	15.22	1.0725	.01508	1.34506	373.1	5.197	22.64	17.54	0.41
Na ₃ PO ₄	17.92	1.0823	.01588	1.34997	386.2	13.68	40.36	26.56	0.61
(NH ₄) ₃ PO ₄	14.62	1.0921	.01649	1.36148	401.7	13.46	41.51	26.74	0.59

values thus calculated are in very good agreement. It must be mentioned that great care was taken in the measurements of the rotation, refractive index and dispersion. The values of the molecular refractivity of the acids and salts are in complete agreement with the results obtained by previous workers. The γ values for 100% HNO_3 and H_2SO_4 are very close to the extrapolated values reported by Darwin and Watson (1927).

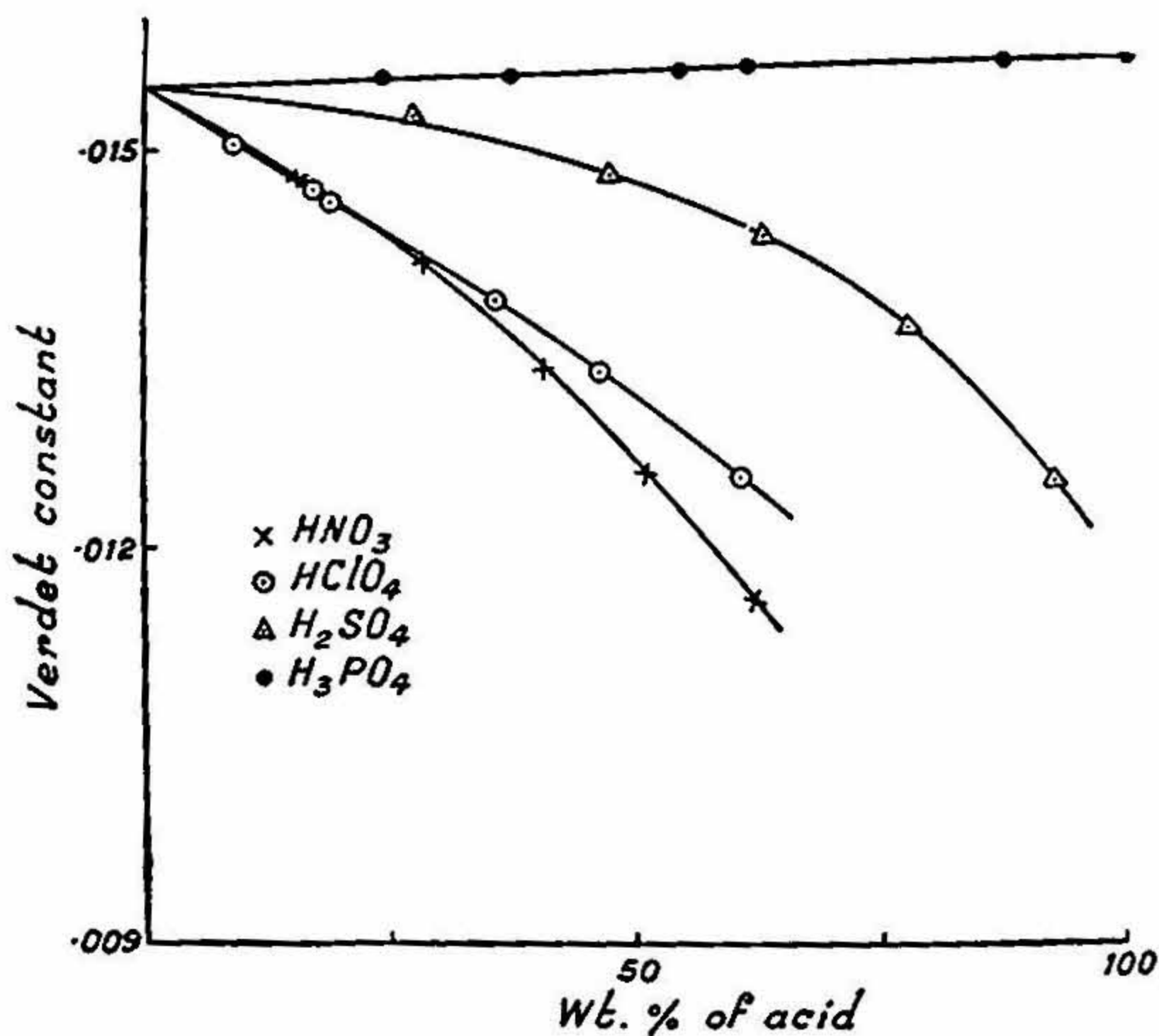


FIG. 1. Variation of Verdet constant with concentration.

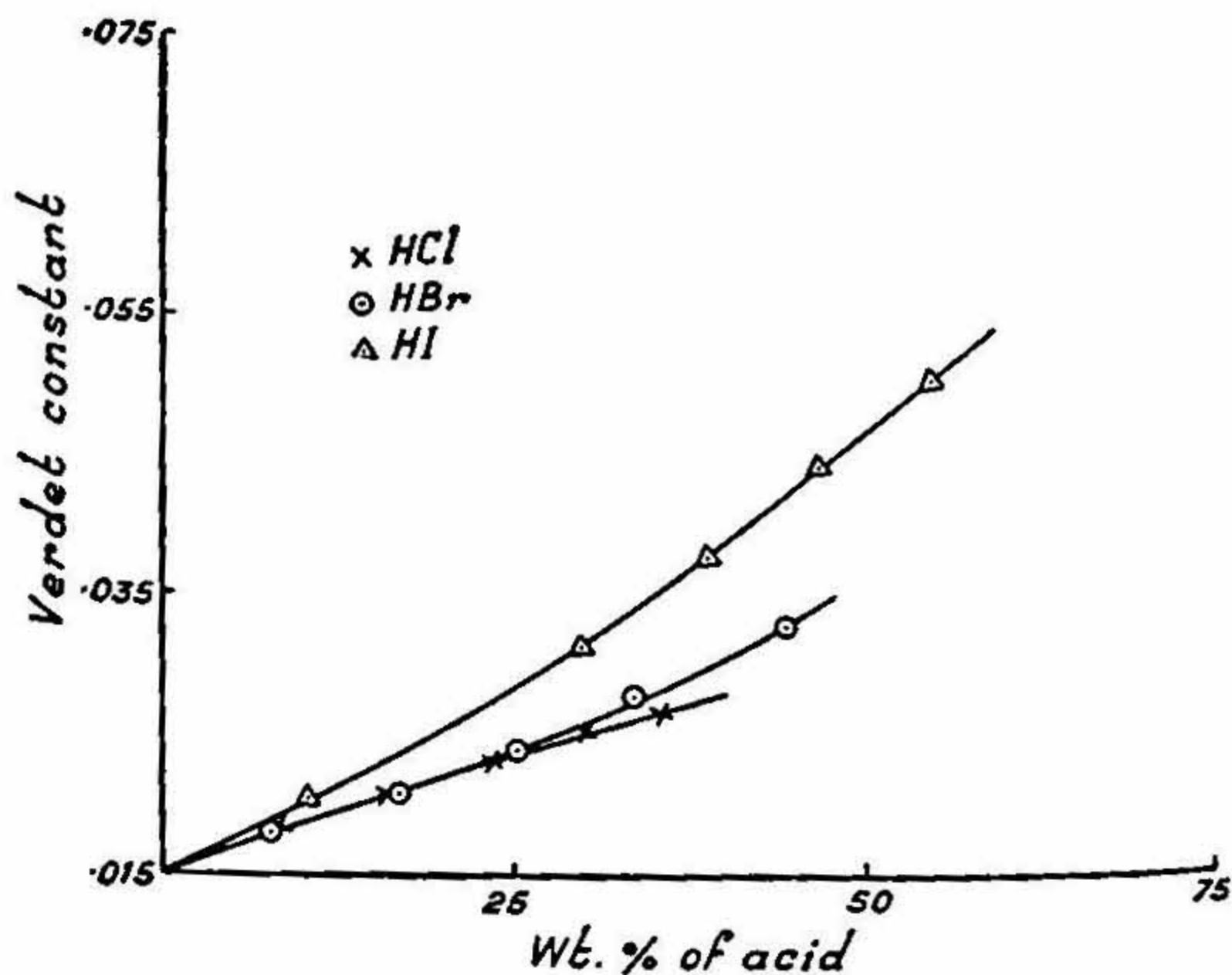


FIG. 2. Variation of Verdet constant with concentration,

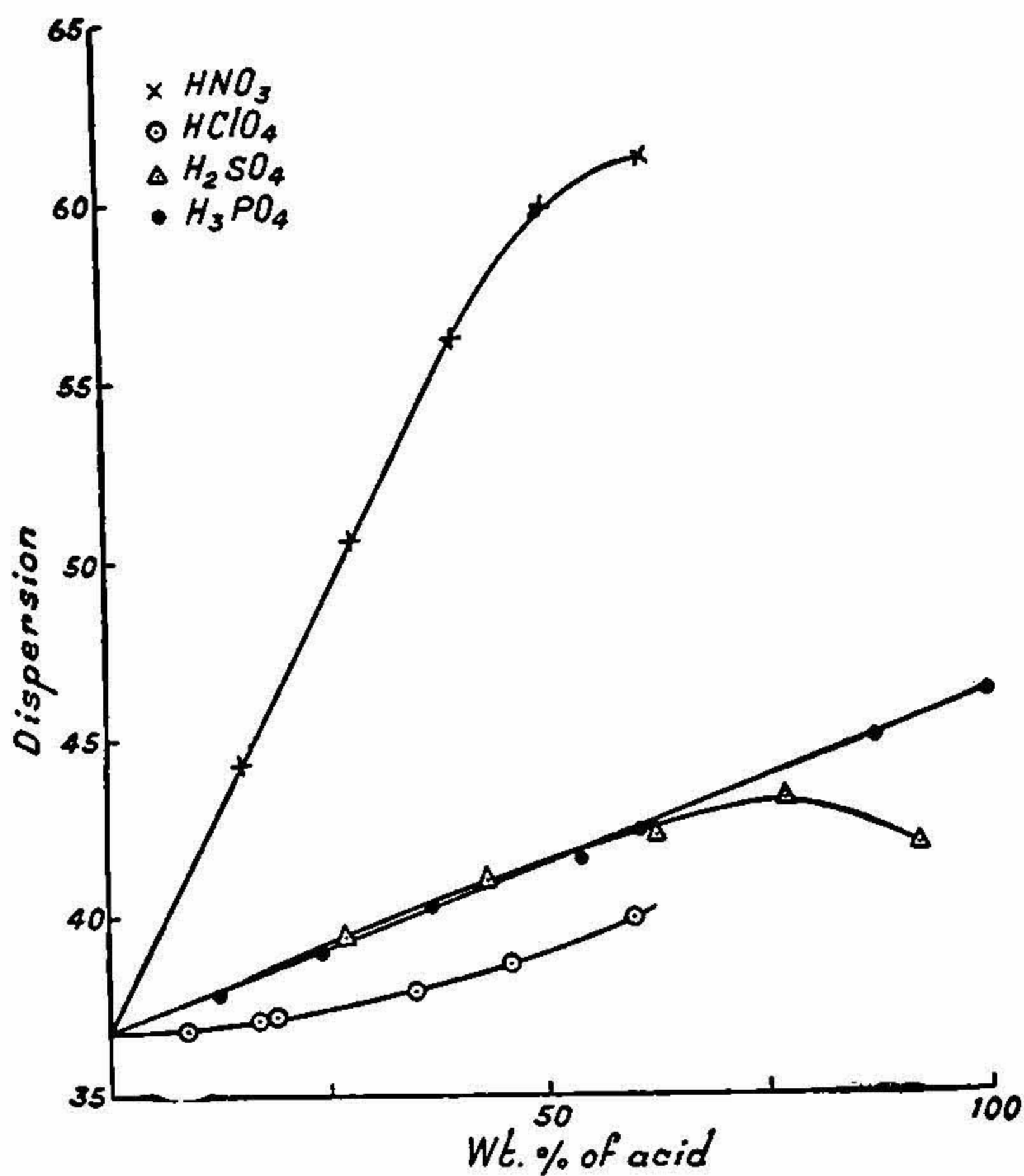


FIG. 3. Variation of dispersion with concentration.

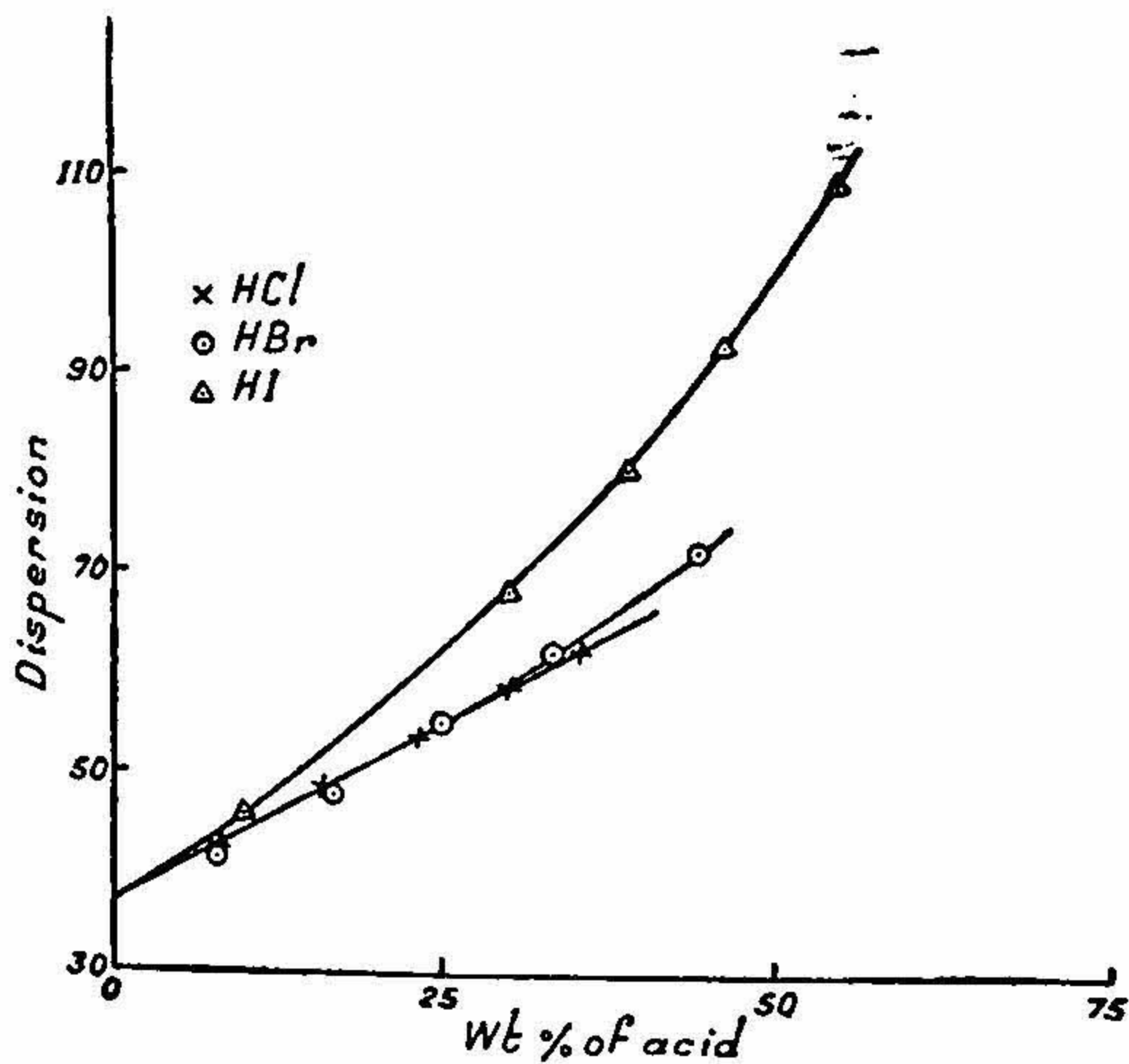


FIG. 4. Variation of dispersion with concentration.

TABLE III. *Magneto-optic anomaly of pure inorganic acids*

Substance	γ
HCl	.79
HBr	.86
HI	.90
HNO ₃	.20
HClO ₄	.38
H ₂ SO ₄	.53
H ₃ PO ₄	.62

4. DISCUSSION

The most striking result obtained in this investigation is the fact that all the acids having ions with strong covalent bonds have γ values much smaller than those for the halogen acids in which the ions have practically the inert gas structure. As it has not yet been possible to get a quantitative relation connecting the strength of binding, covalency, the electronic configuration and the magneto-optic anomaly factor, we shall content ourselves with pointing out certain very interesting features that emerge out of the present investigation.

One notices from the curves that while the Verdet constant in HNO₃ and other acids decreases, the dispersion in these acids increases with increase in concentration. On the other hand, in the case of the halogen acids both the Verdet constant and the dispersion increase with concentration. It is therefore evident that in HNO₃, etc., the near ultra-violet bands while contributing considerably towards dispersion are practically inoperative magneto-optically. This would also explain the low value of γ obtained in the case of these acids. It is proposed to measure the magneto-optic rotation near the absorption bands for it is felt that further studies on the dispersion of magneto-optic rotation would throw some light on this problem.

In the acids it is found that γ (HNO₃) < γ (HClO₄) < γ (H₂SO₄) (< γ H₃PO₄) < γ (HCl) and in the salts also it is in the same order as in the acids. This appears to agree well with R. Serber's (1932) rough rule in the case of molecules, namely that molecules with complicated cores should

have lower values of γ . It may be mentioned that in the case of salts although a small increase in rotativity with concentration was detected, not much weight could be attached to this as the actual magnitude of the total rotation was very small. In all the acids studied here, the magneto-optic rotativity of the ions increases and dispersivity decreases with concentration and hence the anomaly factor increases considerably with concentration, the percentage of increase being most striking in the case of HNO_3 . This systematic increase or decrease may be partly due to the stepwise process of dissociation and hydration that occur at various stages. There is also considerable evidence to show that the ions containing covalent bonds are deformed when the concentration is increased. For instance the comprehensive study of the Raman spectra of metallic nitrates (J. P. Mathieu and N. Lounsbury, 1951) at various concentrations shows that the nitrate ion experiences a deformation which is indicated by the splitting of the ν_3 deformation frequency of the ion at $1370\text{--}1390\text{ cm.}^{-1}$. Further according to Venkateswaran (1936), the NO_3 group changes from a pyramidal form to a plane equilateral type. This is supported by the shift of the Raman frequency from 1297 cm.^{-1} in the acid molecule to 1051 cm.^{-1} in the ion. Similar changes are known to occur in the case of the SO_4^{--} , PO_4^{--} and ClO_4^- ions. For example, the Raman frequencies 409 and 1038 decrease with increasing concentration in H_2SO_4 . Forteyne (1938) has observed the diminution with concentration of the force constants of the perchlorate ion. But in these acids the dissociation and hydration would necessarily introduce other complicating effects.

From these observations, it could be generally concluded, that there is loosening in the structure of the ions with increase in concentration and as the strength of the binding decreases the value of the magneto-optic anomaly factor increases.

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