ART. XXXVIII.—*On the Circular Polarization of certain Tartrate Solutions.* I. By J. H. LONG.

THE change in the circular polarization of a solution of an active substance by admixture with an inactive one has been studied in several cases. Müntz found, for instance, that the specific rotation of cane sugar for a concentration of 20^{gm} in 100^{cc} changed from $[\alpha]_D = 66\cdot^\circ5$ to $[\alpha]_D = 66\cdot^\circ3$ by addition of 5^{gm} of NaCl, and to $61\cdot^\circ0$ by addition of $20^{m}.^{g}$

The same chemist and others have shown the effects of adding various substances to sugar solutions. In most cases a decrease in the specific rotation was found.

Under certain circumstances the addition of an inorganic substance converts an inactive organic body into an active one, as in the case of mannite when in solution with alkalies, weak acids and several neutral salts. Under still other circumstances the rotation of an active body can be very greatly increased by the addition of certain inactive ones, as is well illustrated by Gernez (*Berichte der Deutschen Chem. Gesell.*, xx, Ref. 251), in his experiments on mixtures of tartrates with molybdates, arsenates, tungstates, etc. He found, for instance, that the addition of $NH_4 MoO_4$ to a solution of tartaric acid increased its rotation about fifty times.

This subject is one of great practical interest as well as of scientific importance, and it seemed to me that further investigation on the rotation of the tartrates must yield results of some value.

The following pages discuss results obtained with solutions of Rochelle salt in an investigation begun above a year ago and which is still in progress.*

Apparatus and methods.

In my experiments I employed a new model Laurent instrument made by Schmidt & Haensch, and used with this polarization tubes 200 and 220^{mm} in length, surrounded by a water jacket. The tubes were carefully measured and were found to differ so slightly from the given length (less than ·05^{mm}), that I employ the whole numbers instead of introducing a fraction in the calculations. By means of suitable appliances the temperature of the solutions under examination was kept within 0°·2 of 20°, as shown by a delicate thermometer. In most cases, however, this extreme accuracy in the control of the temperature was not necessary as the variations caused by change of temperature were very small. In each test a dozen or more readings were made for each position of the analyzing Nicol, and on the two verniers 180° apart. The instrumental error was almost inappreciable to begin with, and disappeared entirely by taking a mean of all the readings.

At a temperature of 20° a solution of tartaric acid containing 15^{gm} in 100^{cc} showed a specific rotation $[\alpha]_D = 13°·03$. This is diminished when the solution contains free mineral acids, and is also much diminished when certain neutral salts are added. With a solution containing 15^{gm} of tartaric acid and 8^{gm} of sodium chloride I found the specific rotation less than one-half as much as before, viz: $[\alpha]_D = 6°·16$.

If instead of starting with tartaric acid a neutral tartrate be taken and various salts added quite different results are obtained. In the first place, the change in the specific rotation is much less than when the acid is used, and besides this the na-

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* This investigation was begun before the work of Gernez came to my notice, and before the publication of recent papers by Landolt (Berichte, 1888, p. 191), in which reference is made to the behavior of certain tartrates. A second paper will deal with other tartrate solutions.

ture and amount of the change is characteristic of certain groups of salts. These points are shown below.

At the outset I prepared a quantity of pure Rochelle salt, sufficient for all experiments contemplated, and determined the rotation with five solutions containing exactly 5, 15, 25, 35 and 45^{gm} in 100^{cc}, measured at 20° C.

The results of these tests are given in the table, the specific rotation being calculated from the formula,

$$[\alpha] = \frac{10^4\ \alpha}{L.\ C.},$$

in which α is the observed angle of rotation, L the length of the tube containing the solution in millimeters, and C the concentration of the solution, that is, the number of grams in 100^{cc}.

T	L	C	Sp. Gr. $(\frac{20}{4})$	α	$[\alpha]$
20°	200^{mm}	5	1·0261	2°·214	22°·14
20°	200^{mm}	15	1·0739	6°·650	22°·16
20°	200^{mm}	25	1·1202	11°·058	22°·12
20°	200^{mm}	35	1·1655	15°·493	22°·13
20°	200^{mm}	45	1·2100	19°·854	22°·06

The specific rotation appears to be practically constant with the varying concentration, and the change in the angle of rotation by variation of temperature is inappreciable as I found by observing several of the solutions when heated to 35°. Krecke found (*Arch. Néerland.*, vii, 202), with a Rochelle salt solution containing 20^{gm} in 100^{cc}, the specific rotation $[\alpha]_D = 22°{\cdot}42$ at 25° C. For a solution containing $10{\cdot}771^{gm}$ of the anhydrous salt in 100^{cc} Landolt found (*Berichte*, vi, 1073), $[\alpha]_D = 29°{\cdot}67$, which is equivalent to 22°·09 for the crystals.

This is practically the same as I obtained in the table above, and as I found it in numerous other tests carefully conducted I am inclined to think it is the true specific rotation. In what follows I will take 22°·1 as the constant at 20°.

For each one of the following tests I took 20^{gm} of the Rochelle salt and dissolved it in a narrow-necked flask graduated to hold 100^{cc} at 20°. Then the amount of the inactive salt was added and water enough to nearly reach the mark. After shaking, the flask was brought to the right temperature by suspending it in a large vessel of water kept at 20°. A little distilled water having the same temperature was added and this was continued, until, after shaking, the mark was just reached. The limit of error here is about one-twentieth of one per cent.

The solutions so made were then used in the polariscope. In all the experiments here given the temperature was kept at 20° and the 200^{mm} tube was employed.

The following table embraces the results obtained:

Formula and amount of inactive salt added to 20gm. of KNa $C_4H_4O_6.4H_2O$ in 100cc.		Observed rotation α	Specific rotation [α]	Deviation from Normal.
NaCl	5gm	8°·719	21°·80	—°·30
NaCl	10	8·483	21·21	— ·89
NaCl	15	8·218	20·54	—1·56
NaCl	20	7·900	19·75	—2·35
NaBr	5	8·757	21·89	— ·21
NaBr	10	8·668	21·67	— ·43
NaBr	15	8·558	21·40	— ·70
NaBr	20	8·440	21·10	—1·00
Na_2SO_4 (anhyd.)	5	8·669	21·67	— ·43
Na_2SO_4	10	8·526	21·32	— ·78
Na_2SO_4	15	8·376	20·94	—1·16
Na_2SO_4	20	8·200	20·50	—1·60
$NaNO_3$	5	8·688	21·72	— ·38
$NaNO_3$	10	8·604	21·51	— ·59
$NaNO_3$	15	8·514	21·29	— ·81
$NaNO_3$	20	8·426	21·07	—1·03
$Na_2HPO_4 . 12H_2O$	5	8·765	21·91	— ·19
$Na_2HPO_4 . 12H_2O$	10	8·721	21·80	— ·30
$Na_2HPO_4 . 12H_2O$	15	8·675	21·69	— ·41
$Na_2HPO_4 . 12H_2O$	20	8·630	21·58	— ·52
$Na_2S_2O_3 . 5H_2O$	5	8·744	21·86	— ·24
$Na_2S_2O_3 . 5H_2O$	10	8·611	21·53	— ·57
$Na_2S_2O_3 . 5H_2O$	15	8·497	21·24	— ·86
$Na_2S_2O_3 . 5H_2O$	20	8·365	20·91	—1·19
$NaH_2PO_2 . H_2O$	5	8·761	21·90	— ·20
$NaH_2PO_2 . H_2O$	10	8·575	21·44	— ·66
$NaH_2PO_2 . H_2O$	15	8·360	20·90	—1·20
$NaH_2PO_2 . H_2O$	20	8·127	20·32	—1·78
$NaC_2H_3O_2 . 3H_2O$	5	8·782	21·95	— ·15
$NaC_2H_3O_2 . 3H_2O$	10	8·681	21·70	— ·40
$NaC_2H_3O_2 . 3H_2O$	15	8·566	21·41	— ·69
$NaC_2H_3O_2 . 3H_2O$	20	8·450	21·12	— ·98
$Na_2B_4O_7 . 10H_2O$	10	8·729	21·82	— ·28
Na_2WO_4 (anhyd.)	10	8·276	20·69	—1·41
LiCl (anhyd.)	6·752	8·172	20·43	—1·67
Tl_2SO_4	5	7·469	18·67	—3·43
KCl	5	9·088	22·72	+ ·62
KCl	10	9·140	22·85	+ ·75
KCl	15	9·228	23·07	+ ·97
KCl	20	9·372	23·43	+1.33
KBr	5	9·087	22·72	+ ·62
KBr	10	9·123	22·81	+ ·71
KBr	15	9·172	22·93	+ ·83
KBr	20	9·244	23·11	+1·01
KI	5	8·918	22·29	+ ·19
KI	10	9·025	22·56	+ ·46
KI	15	9·105	22·76	+ ·66
KI	20	9·182	22·95	+ ·85
KNO_3	5	8·986	22·46	+ ·36
KNO_3	10	9·104	22·76	+ ·66
KNO_3	15	9·239	23·10	+1·00
KNO_3	20	9·387	23·47	+1·37

Formula and amount of inactive salt added to 20gm. of KNa $C_4H_4O_6.4H_2O$ in 100cc.		Observed rotation a	Specific rotation $[a]$	Deviation from Normal.
KSCy	5	8·994	22·48	+ ·38
KSCy	10	9·030	22·58	+ ·48
KSCy	15	9·075	22·69	+ ·59
KSCy	20	9·134	22·83	+ ·73
$KC_2H_3O_2$	5	9·008	22·52	+ ·42
$KC_2H_3O_2$	10	9·093	22·73	+ ·63
$KC_2H_3O_2$	15	9·160	22·90	+ ·80
$KC_2H_3O_2$	20	9·248	23·12	+1·02
K_2SO_4	5	9·040	22·60	+ ·50
K_2SO_4	10	9·094	22·73	+ ·63
$K_2C_2O_4 . H_2O$	5	9·030	22·57	+ ·47
NH_4Cl	5	9·033	22·58	+ ·48
NH_4Cl	20	9·239	23·10	+1·00
NH_4Br	5	8·987	22·47	+ ·37
NH_4Br	15	9·093	22·73	+ ·63
$(NH_4)_2C_2O_4 . H_2O$	5	9·004	22·51	+ ·41
NH_4SCy	10	9·036	22·59	+ ·49

A simple inspection of the table shows immediately several important points. The addition of the sodium salts, without exception, causes a decrease in the rotation, which is greater as the amount of inactive salt is increased. The behavior of the thallium salt is interesting; here a remarkable change is produced. Experiments now in progress promise to throw some light on the action of thallium compounds in parallel cases. The addition of potassium and ammonium salts, without exception, increases the specific rotation. This deviation becomes greater as more of the inactive salt is added. We have here a remarkable difference between the sodium, thallium and lithium compounds on the one hand and the potassium and ammonium compounds on the other. These peculiarities may sometimes be applied in the quantitative analysis of salt mixtures. These characteristic points and the amount of variation can be most conveniently shown by curves in which the abscissas are the amounts of inactive substance in solution with 20^{gm} of Rochelle salt and the ordinates the specific rotation of the mixture, or better, the deviation of this from a simple water solution of the tartrate.

I have drawn the curves given in fig. 1 on this plan. It will be observed that some of them are practically straight lines which can be represented by a simple equation of the form

$$[\alpha] = (\alpha)_0 + Ag,$$

in which g is the amount of inactive substance in solution, and $(\alpha)_0$ the calculated rotation when $g = 0$. It might appear that this value should be the same as that observed for the pure tartrate solution, but I think that does not necessarily follow.

In the other cases the observations lead to a curve as expressed by

$$[\alpha] = (\alpha)_0 + Ag + Bg^2,$$

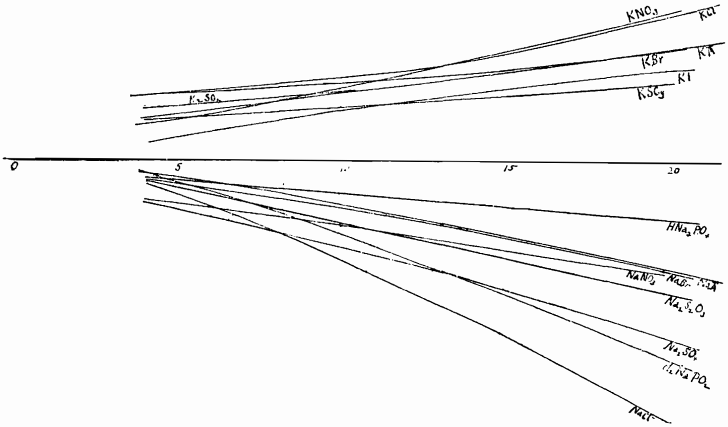
in which the letters have the same meaning as before.

From the first three solutions containing potassium nitrate I have calculated according to this

$$[\alpha] = 22{\cdot}^\circ 20 + 0{\cdot}048g + 0{\cdot}0008g^2.$$

I have not thought it necessary to find an interpolation formula for all the solutions. It is evident from an inspection of the curves that they intersect the base line at $g = 0$ only in a few instances, and the deviations are usually greater than could be referred to errors of observation.

1.



As mentioned above, the addition of a potassium salt increases the rotation while sodium salts diminish it. The numbers as given seem to show no relation beyond this. However, if instead of giving the rotation for solutions containing equal weights of active and inactive substance, they be calculated for equal numbers of molecules in solution the results obtained show certain regularities which must be more than accidental. These desired values can be obtained readily and accurately by graphic interpolation and in the following table they were so derived.

$[\alpha]$, *When for* 1 *molecule of tartrate* 1, 2 *or* 3 *molecules of inactive substance are present.*

Formula of salt.	1 mol.	2 mol.	3 mol.	
$NaCl$	21·86	21·41	20·99	
$NaBr$	21·79	21·42		
$NaNO_3$	21·68	21.41	21·16	
Na_2SO_4	21·32	20·49		
$Na_2HPO_4 . 12H_2O$	21·40			
$Na_2S_2O_3 . 5H_2O$	21·07			(For ½ mol. = 21·61)
$NaH_2PO_2 . H_2O$	21·67	20·92		(For 1½ mol. = 21·41)
$NaC_2H_3O_2 . 3H_2O$	21·72	21·16		
KCl	22·73	22·88	23·14	
KBr	22·78	23·00		
KI	22·63	23·09		
KNO_3	22·60	23·07		
$KSCy$	22·52	22·66	22·82	
$KC_2H_3O_2$	22·60	22·87	23·25	
K_2SO_4	22·79			
NH_4Cl	22·54	22·67	22·81	
NH_4Br	22·54	22·70		

We see from the above that the specific rotation in presence of two molecules of $NaCl$, $NaBr$, $NaNO_3$, or one molecule of $Na_2HPO_4 . 12H_2O$, or one and one-half molecules of $NaH_2PO_2 . H_2O$ is very nearly the same, 21·°41.

In presence of one molecule of Na_2SO_4 it is a little less, while for $NaC_2H_3O_2$ and $Na_2S_2O_3$ no simple relation is apparent.

Two molecules of KBr, KCl, KI, KNO_3 and $KC_2H_3O_2$ exert nearly the same influence, one molecule of K_2SO_4 gives a smaller value, while $KSCy$ is irregular.

Roughly, it appears that the potassium salt molecules increase the rotation in about the same proportion that the sodium salts diminish it. The explanation of this may not be immediately apparent.

Cases similar to those observed in the experiments of Gernez, referred to above, have been explained by the hypothesis of Biot according to which loose combinations are formed between the active and inactive substance having a rotation different from that of the former. Gernez has given the composition of some of these molecular combinations. The case in hand, however, is somewhat different. If we could assume here an action of mass by which on addition of potassium salts the solution would be made to contain neutral potassium tartrate, and on addition of sodium salts neutral sodium tartrate, then the disturbance could be partially explained. According to Landolt (*Ber.*, vi, 1073), the specific rotation of neutral potassium tartrate, calculated as anhydrous, is 28·48, while that of the neutral sodium salt is 30·85. However, if instead of taking equal weights as our basis we take equal numbers of molecules, we obtain the following values representing the *molecular rotation* of the three salts,

$$\begin{aligned} K_2C_4H_4O_6 &= 64{\cdot}42 \\ KNaC_4H_4O_6 &= 62{\cdot}34 \\ Na_2C_4H_4O_6 &= 59{\cdot}85 \end{aligned}$$

from which it is apparent that the conversion of 20^{gm} of Rochelle salt into the neutral potassium tartrate would give a solution with increased rotation, while conversion into sodium tartrate would give a solution with diminished rotation. On this assumption the change can be accounted for in part, but only in part. Taking the rotation for the mixture of 20^{gm} of $KNaC_4H_4O_6 . 4H_2O$ with 20^{gm} of KCl, given in the table above, we have $\alpha = 9^\circ{\cdot}372$. Now, considering this as produced by $16{\cdot}03^{gm}$ of $K_2C_4H_4O_6$—the equivalent of 20^{gm} of $KNaC_4H_4O_6 . 4H_2O$—we obtain a specific rotation,

$$[\alpha] = 29^\circ{\cdot}23,$$

which is too much, Landolt's value being 28·48.

In the same way taking the rotation $\alpha = 7^\circ{\cdot}900$ found for the solution containing 20^{gm} of $KNaC_4H_4O_6 . 4H_2O$ and 20^{gm} of NaCl and supposing this rotation produced by $13{\cdot}76^{gm}$ of $Na_2C_4H_4O_6$ we find the specific rotation,

$$[\alpha] = 28{\cdot}70,$$

which is too low, or, in other words, *too great a reduction*, Landolt's value being 30·85.

It will be seen, however, that the rotations found for the mixtures of the tartrate with the equivalent of two molecules of the simpler inactive salts give numbers which agree with Landolt's values. This is probably more than a mere coincidence. I am at present making a somewhat closer study of it.

The above mentioned hypothesis, while not adequate to explain fully the difference in behavior between the inactive salts added to the tartrate, is still worthy of consideration, I think. In the further progress of the work I shall test it fully. The phenomenon is evidently a complex one and a study of the behavior of other double tartrates must be made before it can be thoroughly understood.

Preliminary experiments indicate that the double tartrates containing thallium or antimony will well repay investigation. The necessary material for such a study is now in course of preparation by an assistant in my laboratory, and with this I hope to be able to throw more light on the subject.

Chicago, July 18th, 1888.