

CCCLXIX.—*Optical Rotatory Powers of d-β-Octyl Hydrogen Phthalate and its Salts in Various Concentrations, and the Influence of Added Electrolytes.*

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SINCE 1873, when Landolt examined the rotatory powers of tartaric acid and its derivatives, optically active acids and their salts have been the subject of many detailed investigations. From these it has emerged that the Landolt–Oudemans law does not hold in its original simplicity and that the characteristic influence of the positive ion in the salts may in some cases persist even at high dilutions. In addition, it has been discovered that added electrolytes frequently induce specific changes in the rotatory powers of the acids and their salts.

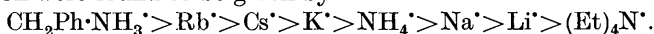
Apart from a few investigations on α -bromocamphor- π -sulphonic acid, practically all these researches have dealt with hydroxy-acids. Stubbs (J., 1911, **99**, 2284) has reviewed and extended the data obtained by Schneider in 1881 for the rotatory power of *l*-malic acid in aqueous solution.

In discussing the shift towards a positive rotation resulting from the addition of various chlorides, Stubbs concludes that for univalent kations the magnitude of the displacement is in the order of their electro-affinities, *viz.*, Cs > Rb > K > Na > NH₄ > Li > H. For bivalent ions the arrangement is Ba > Ca > Mg > Cd > Zn > Hg, among which $\frac{1}{2}$ Ba and $\frac{1}{2}$ Ca have an effect greatly exceeding that of Cs. Mercuric chloride only produces an insignificantly small change. Among the acid and neutral salts of malic acid, the negative molecular rotations are in the order Li > Na > K.

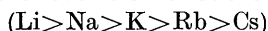
Stubbs advances no very definite suggestions as to the nature of the ionic influence, but surmises that it may be connected with the presence of an alcoholic hydroxyl group in the molecule of malic acid. It is noted that when the hydroxyl is definitely attacked and a chemical complex formed, the great sensitiveness of the acid to

changes of concentration disappears (Rosenheim and Itzig, *Ber.*, 1899, **32**, 3432). Similar though less comprehensive results have been obtained for tartaric acid by Clough (*J.*, 1914, **105**, 49) and by Patterson and Anderson (*J.*, 1912, **101**, 1833), who also observed that the rotatory power of homogeneous ethyl tartrate was affected in much the same manner by the addition of neutral salts.

More recently, Darmois (*Ann. Physique*, 1928, **10**, 70; *Trans. Faraday Soc.*, 1930, 384) has studied various organic and inorganic salts of tartaric acid and the effect of added salts. The positive rotations of the tartrates at moderate concentrations in aqueous solution were found to be given by

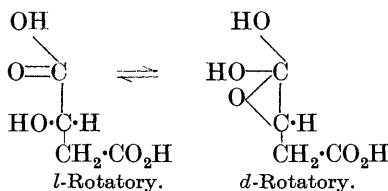


Of these, the first five raise the rotatory power with respect to the tartaric ion at extreme dilutions, and the remaining salts have lower values. Added halides influence the rotation of sodium tartrate in the sense $\text{K} > \text{Na} > \text{Cd} > \text{Mg} > \text{Ca}$, the highest value being given in the presence of potassium chloride. These results are in the main interpreted on the assumption that the electronic orbits in the tartrate ion are deformed by the oppositely charged positive ions, the greater the deformation the higher being the positive rotatory power. The optical effect of the univalent ions of the alkali metals is concluded to be in the reverse order of their ionic radii



as calculated from ionic mobility with the aid of Stokes's formula. Owing to its high degree of hydration, the lithium ion has the greatest radius and thus exerts a diffused electric field; whereas the rubidium and caesium ions are less hydrated, and their fields more intense. In a similar manner the tetraethylammonium ion is strongly hydrated and brings about a small deformation as compared with the benzylammonium ion, which exists in the unhydrated state.

In an investigation dealing with malic acid, Bancroft and Davies (*J. Physical Chem.*, 1930, **34**, 897) attribute the optical sensitiveness towards concentration and other changes in environment to the presence of the free hydroxyl group attached to the asymmetric

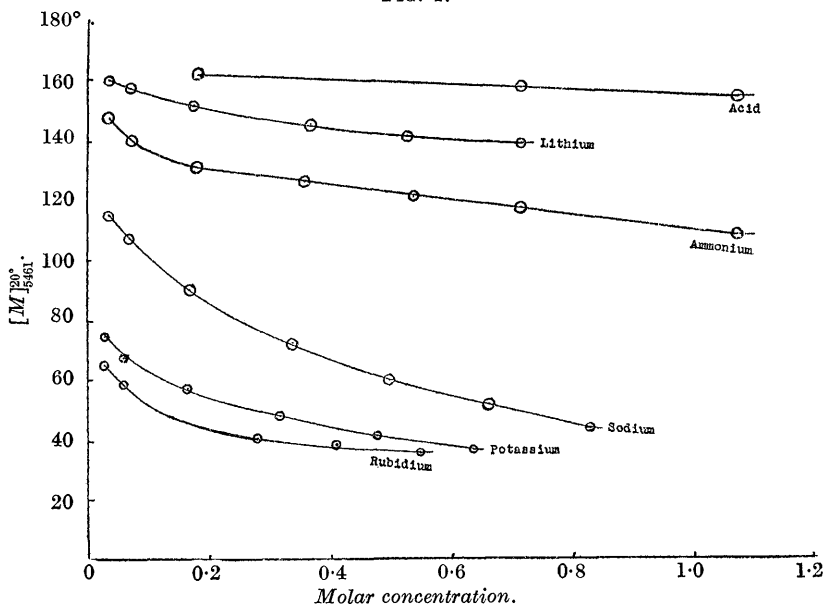


atom. These authors assume the existence of two tautomeric forms of malic acid, *viz.*, the normal structure, which is *l*evorotatory, and

an ethylene-oxide form which is held to be responsible for the dextrorotation in concentrated solutions. This hypothesis is open to criticism on the ground that it requires the ethylene-oxide structure to be formed in the presence of concentrated hydrochloric acid, a reagent which brings about a strong dextrorotation.

α -Bromocamphor- π -sulphonic acid and its salts (Walden, *Z. physikal. Chem.*, 1894, **15**, 196; *Monatsh.*, 1929, **53**, 14; Campbell, Thesis, Edinburgh, 1930; *J. Physical Chem.*, 1931, 1143) undergo little variation in rotatory power with change of concentration, and

FIG. 1.



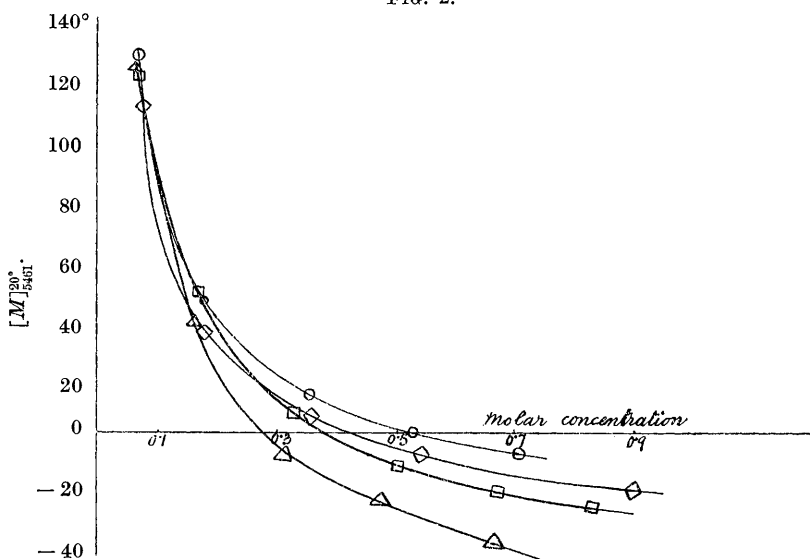
d-sec.- β -Octyl hydrogen phthalate and salts. Alcoholic solutions.

exhibit few regularities under the influence of added salts. Campbell, however, finds that with alkali halides, the rotatory powers show very small differences in the order $K > Na > Li$, and also inclines to the view that the changes of greater magnitude observed by other investigators are dependent on the presence of alcoholic hydroxyl groups in the optically active solute.

In order to obtain further evidence bearing upon this problem, an examination has now been made of the alkali and ammonium salts of *d*- β -octyl hydrogen phthalate under various conditions. These derivatives contain no alcoholic hydroxyl groups and the only polar complexes present are those derived from carboxylic groups.

Owing to the insolubility of the free acid, the concentration effects could not be studied in aqueous solution, but the results obtained in alcohol show that the rotatory power is only influenced in a minor degree by change of concentration. The observed values of $[M]_{5461}^{20}$ for alcohol, together with those relating to various salts in the same solvent are illustrated in Fig. 1. For a concentration of 0.5*M*, they range from 160° for the free acid to 37° for the rubidium salt, and fall into the order (H) > Li > NH₄ > Na > K > Rb. In aqueous solution (Fig. 2), the rotations for the different salts lie

FIG. 2.



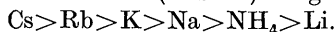
d-sec.-β-Octyl hydrogen phthalate. Aqueous solutions of alkali salts.

○ Lithium. ◇ Ammonium. □ Sodium. △ Potassium.

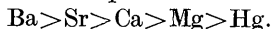
closely together at concentrations below $c = 5$ (0.167*M* for the sodium salt), but at somewhat higher concentrations they exhibit characteristic differences of the same nature as those found for alcoholic solutions. Eventually, the values for aqueous solution become reversed in sign. A similar salt effect, (H) > Li > Na > K, which also involves an inversion in sign, has recently been recorded for salts of *l*-menthyl hydrogen naphthalate in methyl alcohol (Rule and McLean, this vol., p. 669).

These changes in rotatory power due to the varying nature of the metallic or other positive radical present in the active solute are repeated when sodium *d*-octyl phthalate is examined in water or aqueous alcohol containing neutral added salts. Here again the

displacements towards a negative value caused by univalent ions derived from the alkali chlorides (Table I) are given by



This series is identical with that deduced above for the rotatory powers of the corresponding *d*-octyl phthalates. It is also identical, even to the position of NH_4 , with the series found by Stubbs for the influence of added salts upon free malic acid. The resemblance to the case of malic acid is still further emphasised by the changes due to bivalent ions, which for the phthalate are in the order



For malic acid Stubbs records $\text{Ba} > \text{Ca} > \text{Mg} > \text{Hg}$. In both series the depression due to the comparatively un-ionised mercuric salt is negligible, and those due to the alkaline-earth metals are much greater than for equivalent amounts of the univalent alkalis. As may be seen from Table I, the influence of a salt in depressing the rotatory power becomes relatively greater in more dilute solution. In this and other tables, *M* denotes the molarity of the halide.

TABLE I.

Influence of added electrolytes upon the rotatory power of sodium d-β-octyl phthalate (0.2M in water; l = 2).

Halide.	<i>M</i> .	α_{5461} .	$[\alpha]_{5461}$.	Δ .
None	—	+1.35°	+11.24°	—
LiCl	0.5	-0.04	- 0.33	-11.6
NH ₄ Cl	0.5	-0.19	- 1.58	-12.8
NaCl	0.5	-0.58	- 4.83	-16.1
KCl	0.5	-1.06	- 8.82	-20.1
RbCl	0.5	-1.31	-10.9	-22.1
CsCl	0.5	-1.79	-14.9	-26.1
KCl	0.05	+0.78	+ 6.5	- 4.8
KCl	0.10	+0.38	+ 3.2	- 8.2
CsCl	0.05	+0.51	+ 4.2	- 7.1
BaCl ₂	0.05	+0.13	+ 1.1	-10.1
BaCl ₂	0.0375	+0.31	+ 2.6	- 8.6
BaCl ₂	0.025	+0.54	+ 4.5	- 6.8
BaCl ₂	0.0125	+0.92	+ 7.7	- 3.5
SrCl ₂	0.0375	+0.37	+ 3.1	- 8.1
SrCl ₂	0.025	+0.56	+ 4.7	- 6.5
CaCl ₂	0.0375	+0.47	+ 3.9	- 7.3
CaCl ₂	0.025	+0.66	+ 5.5	- 5.7
MgCl ₂	0.05	+0.38	+ 3.2	- 8.0
MgCl ₂	0.0375	+0.59	+ 4.9	- 6.3

In aqueous alcohol (1 : 1 by vol.) (0.2M; l = 2).

None	—	+5.37	+44.7	—
CsCl	0.05	+4.78	+39.8	- 4.9
CdCl ₂	0.025	+5.10	+42.5	- 2.2
HgCl ₂	0.025	+5.31	+44.2	- 0.5

Discussion of Results.

Owing to the insolubility of octyl hydrogen phthalate in water, the concentration changes observed in the case of the free acid were

limited to those occurring in alcoholic solution. The salts, however, could be examined in aqueous and in alcoholic solution, and in both instances underwent considerable variations in rotatory power. The magnitude of the effect in water at high dilutions is probably due in some part to aqueous hydrolysis.

The regular and very definite changes in rotation produced by the addition of neutral salts indicate clearly that this behaviour is not in any way peculiar to optically active hydroxy-acids, as has been assumed by a number of investigators. In this respect *l*-malic acid and *d*-octyl hydrogen phthalate present so complete a parallel as to suggest that the basic cause is to be traced to the only structural factor common to the two molecules, *viz.*, the carboxyl group. The hypothesis advanced by Darmois (*loc. cit.*) for the salts of tartaric acid, according to which the optical variations are due to a deformation of the active ion under the influence of the added kation, may be applied equally to the cases under consideration. Similarly, the observation of Patterson and Anderson, that homogeneous tartaric ester undergoes variations of the same nature, may be explained by assuming that the presence of the polar salt brings about corresponding deformations in the characteristic dipoles of the carbethoxyl or hydroxyl groupings. From this standpoint there is no essential difference between the added salt effects and those resulting from the addition of polar solvents. The greater differences observed between the various alkali salts in alcoholic as compared with aqueous solutions appear to be in agreement with the statement of Darmois that the electrical effects are increased in the medium of lower dielectric constant.

The direction of the change in rotation which occurs when the salts of octyl hydrogen phthalate are examined at increasing concentrations is in the sense to be expected on the assumption of an ionic influence. With rising concentration the probability of deformation due to the proximity of the oppositely charged ions will increase, and the rotatory power will fall.

The large variations which have been observed in the rotatory powers of α -hydroxy-acids with change of concentration are possibly related to alterations in the molecular state. As is well known, hydroxy- and carboxy-derivatives possess highly developed powers of association, both amongst themselves and with each other, and considerable changes may be expected to occur as the association complexes of the hydroxy-acid break down in the presence of a strongly dissociating solvent such as water.

Levene and Rothen (*J. Physical Chem.*, 1930, 2579), from a detailed investigation of mandelic acid and a consideration of the properties of other known active acids, have formulated the general

rule that the change in rotation of an optically active acid (or of its ion) produced by the kations of neutral salts is in the same sense as that observed on passing from the active ion to the active molecule. No support for this generalisation is to be found in the properties of *d*- β -octyl hydrogen phthalate. The changes produced by added kations are in this case towards a lævorotation, and thus in the contrary direction to that found on passing from the active ion to the active molecule.

In the following communication it is shown that octyl hydrogen phthalate undergoes optical changes of the same order and sign in the presence of highly polar solvents, especially those of aromatic type.

EXPERIMENTAL.

The *d*- β -octyl hydrogen phthalate employed was prepared by the method of Pickard and Kenyon (J., 1907, **91**, 2058; 1922, **121**, 2540). Alkali salts of the acid were obtained by titrating an aqueous or alcoholic solution of the compound with a solution of the required

Solvent. <i>l.</i>	<i>M.</i>	$\alpha_{5461}^{20^\circ}$	$[M]_{5461}^{20^\circ}$	Solvent. <i>l.</i>	<i>M.</i>	$\alpha_{5461}^{20^\circ}$	$[M]_{5461}^{20^\circ}$
<i>Lithium d-β-octyl phthalate.</i>				<i>Ammonium d-β-octyl phthalate.</i>			
C ₂ H ₆ O	4	0.035	+ 2.26° + 160°	C ₂ H ₆ O	4	0.036	+ 2.13° + 147.5°
"	2	0.070	+ 2.22 + 157.5	"	2	0.072	+ 2.01 + 139.5
"	2	0.176	+ 5.36 + 152.2	"	1	0.183	+ 2.40 + 131.3
"	1	0.369	+ 5.39 + 146.2	"	1	0.360	+ 4.57 + 126.9
"	1	0.528	+ 7.53 + 142.6	"	1	0.539	+ 6.61 + 122.7
"	1	0.717	+ 10.08 + 140.7	"	1	0.719	+ 8.57 + 119.2
H ₂ O	2	0.070	+ 1.79 + 127	"	1	1.078	+ 11.95 + 110.9
"	1	0.176	+ 0.78 + 44.3	H ₂ O	2	0.072	+ 1.58 + 110
"	1	0.352	+ 0.65 + 12.2	"	1	0.180	+ 0.60 + 33.5
"	1	0.530	± 0.00 ± 0	"	1	0.360	+ 0.20 + 5.6
"	1	0.705	- 0.49 - 6.9	"	1	0.540	- 0.36 - 6.7
"				"	1	0.899	- 1.74 - 19.4
<i>Sodium d-β-octyl phthalate.</i>				<i>Potassium d-β-octyl phthalate.</i>			
C ₂ H ₆ O	4	0.034	+ 1.55 + 115	C ₂ H ₆ O	4	0.032	+ 0.94 + 74
"	2	0.067	+ 1.45 + 107.5	"	2	0.063	+ 0.85 + 67.5
"	1	0.168	+ 1.52 + 90.3	"	2	0.165	+ 1.85 + 57.3
"	1	0.335	+ 2.44 + 72.7	"	1	0.321	+ 1.55 + 48.4
"	1	0.500	+ 2.99 + 59.8	"	1	0.473	+ 1.98 + 41.6
"	1	0.666	+ 3.37 + 52.1	"	1	0.640	+ 2.36 + 36.9
"	1	0.833	+ 3.68 + 44.2				
H ₂ O	2	0.067	+ 1.62 + 120.3	H ₂ O	2	0.064	+ 1.58 + 123
"	1	0.169	+ 0.79 + 46.8	"	1	0.167	+ 0.62 + 37
"	1	0.335	+ 0.21 + 6.3	"	1	0.316	- 0.22 - 7.0
"	1	0.502	- 0.56 - 11.2	"	1	0.474	- 1.10 - 23.2
"	1	0.668	- 1.33 - 19.9	"	1	0.666	- 2.45 - 36.8
"	1	0.833	- 2.08 - 25.0				
Solvent. <i>l.</i>	<i>M.</i>	$\alpha_{5461}^{20^\circ}$	$[M]_{5461}^{20^\circ}$				
<i>Rubidium d-β-octyl phthalate.</i>							
C ₂ H ₆ O	4	0.028	+ 0.73				+ 65.4
"	2	0.055	+ 0.65				+ 58.8
"	1	0.139	+ 0.67				+ 48.0
"	1	0.276	+ 1.14				+ 41.3
"	1	0.413	+ 1.61				+ 38.9
"	1	0.551	+ 1.99				+ 36.1

metallic hydroxide or alkoxide, and using an outside indicator. Finally the solution was evaporated to dryness in a desiccator.

As a check, the solutions were also prepared directly by weighing a definite amount of the acid into a calibrated flask, adding a little water or alcohol and the calculated volume of metallic hydroxide or alkoxide dissolved in the same solvent, and subsequently making up to the mark. The rotations obtained by these two methods agreed within experimental error.

As most of the salts were deliquescent, they were kept in a desiccator, and in order to ensure that the optical properties had undergone no change in the meantime, the rotatory power was again determined at the end of each series of determinations.

In experiments with added salts, the latter were of A.R. quality. Where possible, solutions were made up by weighing out the dried salts, but with deliquescent substances such as magnesium or calcium chloride, the salts were employed in the form of standardised solutions. In the majority of determinations the added salt was present in a concentration of 0.5*M*; in a few cases owing to low solubility smaller concentrations were adopted. Aqueous alcohol was used with mercury and cadmium chlorides in order to prevent precipitation of mercury and cadmium octyl phthalates, which are insoluble in water.

For the sodium salt, no confirmation could be obtained of the existence of a small minimum rotatory power (in alcohol, *M* = 0.6) previously observed by Rule, Miles, and McGillivray (J., 1929, 2274).

Summary.

The rotatory powers of *d*-β-octyl hydrogen phthalate and its alkali salts undergo considerable variations with change of concentration.

Salt formation lowers the rotation of the acid, the relative displacements towards a negative value being represented by Rb > K > Na > NH₄ > Li.

The addition of electrolytes also produces a marked depression in the rotatory power of sodium octyl phthalate. Using various inorganic chlorides, it is found that the depressions resulting from univalent kations fall into the same sequence as that representing the solutions of the homogeneous active salts, *viz.*, Cs > Rb > K > Na > NH₄ > Li. Equivalent amounts of certain bivalent kations produce still greater depressions, in the sense Ba > Sr > Ca > Mg (> Cs), whereas the addition of mercuric chloride, which is relatively un-ionised, only leads to an inappreciable change. These variations are identical in every respect with those observed by Stubbs and by Schneider for *l*-malic acid.

It is therefore concluded that the sensitivity of malic and tartaric acids towards neutral electrolytes and change of concentration is not necessarily related to the presence of alcoholic hydroxyl groups in these compounds, as has been assumed by various investigators, but may be due to the carboxyl group, which is the only structural peculiarity common to these compounds and octyl hydrogen phthalate.

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