285. *Studies in Solvent Action. Part VII. Rotatory Power of Ethyl Tartrate in Relation to the Solvent, Concentration, Degree of Association, and Temperature.*

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A comprehensive survey of the existing data bearing upon the rotatory power of an optically active compound in solution was made nearly 30 years ago by Walden (*Ber.*, 1905, **38**, 390), who suggested that the solvent exerts a two-fold influence, depending partly upon its power of modifying the degree of association of the solute molecules with one another, and partly upon some unknown constitutive property of the medium. Unfortunately, the evidence then available appeared to be inconclusive and contradictory, and the enormous mass of experimental work published since that date has served only to render the issue still more obscure.

Strong support for Walden's views has, however, been advanced in the previous communications of this series (compare this vol., p. **376**), in which the constitutive property in question is identified with the polar character of the solvent, *i.e.*, with the nature and arrangement of the dipoles in the molecule. By employing optically active solutes which do not undergo appreciable self-association in dilute solution, and using, as a further simplification, solvents which are all monosubstituted derivatives of the same hydrocarbon, it is found that the rotatory powers tend to vary sympathetically with the dipole moments of the solvents. This relationship has been interpreted on the assumption that the greater the polarity of the solvent, the greater is the tendency for the solute and solvent molecules to enter into association with, or at least to assume a definite orientation towards, one another. In general, such a departure from an entirely random arrangement of the molecules will lead to a diminution of the field exerted by the dipoles in the optically active molecule and so reduce their contribution to the total rotation.

Additional confirmation of this mechanism has been gained by examining various active compounds at increasing *concentrations* in a non-polar solvent. As was to be expected on the above hypothesis, the change in optical activity was then found to be in the same direction as that observed when a fixed low concentration was employed and the *polarity* of the solvent was increased. The optical displacement thus occurs in the same sense whether the altered conditions result in the active molecules becoming increasingly oriented towards each other, or whether the greater degree of orientation is exhibited by the active molecules towards those of the polar solvent.

In the event of the optically active compounds having a marked tendency towards self-association, it is obvious that a simple relationship between the polarity of the solvent and the rotatory power of the solution will no longer obtain. With such compounds a high degree of molecular orientation (solute–solute type) may occur in non-polar media as well as in those of a highly polar nature (solute–solvent type), leading to similar effects upon the optical rotation. In this case, divergent properties appear to be shown by solvents of zero or low polarity, which are relatively ineffective in dissociating the complexes of the active molecules, and hence yield solutions resembling in their optical properties those given by more strongly polar solvents. An example of this kind was found in β-nitro-octane (*loc. cit.*), which exhibits low rotations, not only in the homogeneous state and in nitrobenzene solution, but also when dissolved in hexane, *i.e.*, under conditions in which it is highly associated with itself or with the solvent. In benzene solution the rotation rose at low concentrations as the degree of association fell off, whilst comparatively high values were observed in the weakly polar anisole.

This communication deals with the behaviour of the more accessible ethyl tartrate. This ester has probably formed the subject of more detailed researches than any other optically active compound, and the discussion is therefore limited to an examination of the optical changes for a fixed wave-length in relation to the polarity of the solvent and the concentration and degree of association of the solute. Even so, much of this ground has been exhaustively investigated by earlier workers, more particularly by Patterson and his collaborators, with whose results the present data are in general agreement. The rotatory powers observed at a concentration of $c = 5$ for solvents of the benzene group are given in Table I, and the influence of changing concentration is shown diagrammatically in Fig. 1.

TABLE I.

Molecular Rotations of Ethyl Tartrate dissolved in Benzene Derivatives ($c = 5, l = 4, t = 20°$).

Solvent.	$[M]_{5461}^{20°}$.	$\mu \times 10^{18}$.	Solvent.	$[M]_{5461}^{20°}$.	$\mu \times 10^{18}$.
s-$C_6H_3(CH_3)_3$	0°	0	C_6H_5Br	+ 21·8°	1·56
$C_6H_5{\cdot}OMe$	+ 5	1·16	C_6H_5Cl	+ 23·0	1·56
$C_6H_5{\cdot}CH_3$	+ 7·4	0·4	$C_6H_5{\cdot}CN$	+ 67·9	3·85
C_6H_6	+ 12·5	0	$C_6H_5{\cdot}NO_2$	+ 80·6	3·90
C_6H_5I	+ 20·2	1·25	$C_6H_5{\cdot}CHO$	+ 100·7	2·75

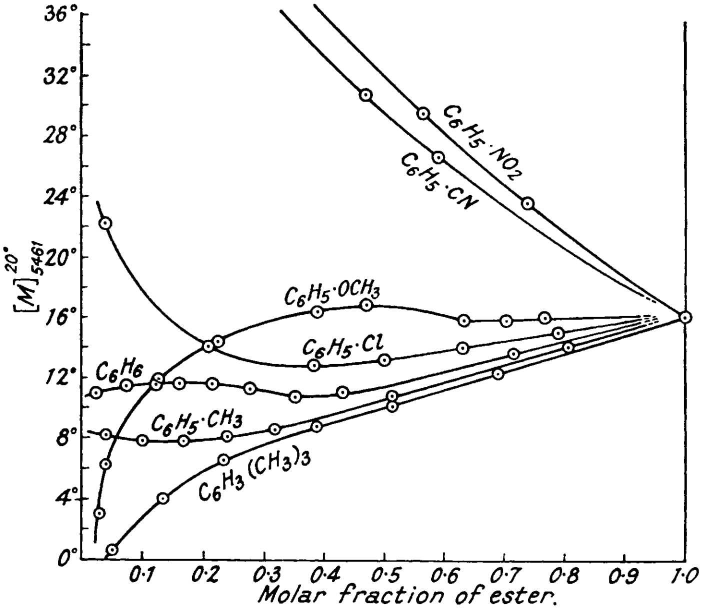
For the homogeneous ester $[M]_{5461}^{20°} = + 16{\cdot}25°$.

From the table, it is evident that a general relationship exists between the rotatory power of the solution and the polarity of the solvent, such that the dextrorotation rises as the dipole moment increases. Anisole and benzaldehyde give somewhat exceptional values, the rotation in the former being lower, and in the latter higher, than that corresponding to the position of the solvent in the polar scale.

More information as to the influence of solvents is obtained by reference to Fig. 1. The changes illustrated may be interpreted in terms of the variations which take place in the electrical environment of the active molecules. At low concentrations in benzene, toluene, and mesitylene, the solute molecules exist for the greater part independently, separated from one another by the non-polar medium. The low rotatory powers observed under such conditions can therefore be regarded as approaching that of the individual ethyl tartrate molecule at the temperature employed. As the concentration of the compound in these solutions is raised, more and more of the tartrate molecules tend at any given moment to be in spatial proximity, and thus to assume a definite orientation towards one another. This change in environment is accompanied by an increase in the dextrorotation, which eventually rises to the value for the comparatively strongly associated homogeneous ester.

FIG. 1.

Molecular rotation of ethyl tartrate in solution.



The passage from the pure ester to a dilute solution in a highly polar solvent such as nitrobenzene similarly represents a progressive change in the same direction and corresponds to a further continuous rise in the rotatory power.

For various reasons, however, the ester molecules in dilute solution in benzene, toluene, or mesitylene cannot be considered to be in a state of *entirely* random orientation. Support for this view may be found, not only in the slope of the mesitylene curve, which still falls rapidly at low concentrations, but also in the various molecular-weight determinations which are recorded in the literature for ethyl tartrate in benzene. A very complete investigation of the latter point was made by Patterson (J., 1902, **81**, 1111), who obtained values by the cryoscopic method ranging from 210 at $c = 0{\cdot}4$ g./100 g. to 344 at $c = 8$. Although the lowest figure approximates to the theoretical (206), it is to be noted that the experimental values rise sharply and continuously from this point, and it may be inferred that, even at the highest dilutions at which it is practicable to determine the rotatory powers, the ester molecules are not free from mutual interaction.* It may therefore be concluded that the optical rotation of the ester dissolved in the aromatic hydrocarbons has suffered a displacement in the dextrorotatory sense owing to the mutual orientation of the solute molecules, thus suggesting one reason for the higher values obtained in these media than in the weakly polar anisole at extreme dilutions. Further support for this view is discussed later in connexion with the behaviour of aliphatic solvents.

An exact comparison between the less polar solvents is complicated by the incidence of maxima and minima in the rotation–concentration diagrams. Irregularities of this kind † have already been shown to exist for benzene and toluene solutions by Patterson (*ibid.*, p. 1099). As may be seen in Fig. 1, the maximum, which is not traceable at all in mesitylene, first becomes visible at the left-hand end of the toluene curve, and shows somewhat more definitely in that of benzene. With the weakly polar solvent anisole, it is displaced further to the right and can be followed over practically the whole of its course. The displacement of the maximum to the right thus increases with the dielectric constant of the solvent as we pass from toluene to anisole, and disappears altogether in more polar media. Owing, apparently, to the magnitude of the maximum in anisole solution, the curve at higher concentrations is in this case elevated above that for chlorobenzene, despite the greater dipole moment of the latter solvent. Attention may be drawn to the fact that, apart from minor irregularities due to the presence of maxima and minima, *the change of rotation which occurs when the concentration of the ester is raised in a non-polar solvent is in the same direction as that observed when a low concentration is employed and the polarity of the medium is increased.* The behaviour of ethyl tartrate thus falls into line with that of various other optically active compounds discussed in Part VI of this series (this vol., p. **376**).

In keeping with its high dipole moment, benzaldehyde yields strongly dextrorotatory solutions. The displacement of this solvent in Table I above the still more polar nitrobenzene and benzonitrile may possibly be due to the secondary effect of co-ordination between the keto-group of the aldehyde and the hydroxyl groups of the ester.

The rotatory powers of the ester in a number of aliphatic solvents have previously been determined over a wide range of concentration by other investigators (cf. Patterson and co-workers, J., 1901, **79**, 167; 1902, **81**, 1097; 1905, **87**, 313; 1908, **93**, 355). Rotations are small, and solvent influences complicated by the existence of maxima and minima. Moreover, in some solvents, notably hexane and carbon disulphide, the low solubilities only permit determinations to be made at high dilutions. The comparison in Table II has therefore been limited to low concentrations.

In general, the arrangement in Table II resembles that for the aromatic group, the tendency being for the less polar solvents to form solutions of lower dextrorotation, with in some cases a reversal in sign. Nitromethane and acetonitrile give more highly dextrorotatory solutions. From the present standpoint, however, the chief interest centres in the behaviour of the non-polar solvents carbon tetrachloride, carbon disulphide, and hexane. Since the active solute is a hydroxy-ester, it was expected that in these solvents it would prove to be appreciably associated and exhibit rotatory powers of intermediate magnitudes (cf. Part VI, *loc. cit.*). Both anticipations are borne out by experiment. Estimations of the molecular weight of the dissolved ester have now been made by the ebullioscopic method using the Menzies–Wright apparatus (*J. Amer. Chem. Soc.*, 1921, **43**, 2309, 2315). No difficulty was experienced in obtaining repeatable values in carbon tetrachloride and carbon disulphide to within 2—4%. Hexane proved less satisfactory as a solvent (cf. Hantzsch, *Ber.*, 1907, **40**, 1560) and slightly larger variations were found in this case, although all the values were higher than those for the above two solvents at

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* Patterson, however, regarded the values as indicating normal molecular weight at low concentrations (*loc. cit.*).

† *l*-Menthyl salicylate in hexane solution behaves in a similar manner (Rule and Dunbar, unpublished). The property appears to be characteristic of many hydroxy-derivatives.

TABLE II.

Molecular Rotatory Powers of Ethyl Tartrate in Simple Aliphatic Solvents ($c = 5$, $l = 4$, $t = 20°$).

Solvent.	$\mu \times 10^{18}$.	$[M]_{5461}$.	M (ebullioscopic method).
$CHCl_3$	1·10	− 11°	235—235 (c, 2·2—9·9); Walden.[3]
CH_2Cl_2	1·61	− 8·6	
Et_2O	1·15	− 4·8	
CCl_4	0	− 0·25[5]	204—227 (c, 1·07—2·62); see Fig. 2.
CH_3I	1·60	+ 1·2	
[1] CS_2	0	+ 6·75	271—447 (c, 2·11—8·51); see Fig. 2.
$CH_3{\cdot}CO_2H$	1·4	+ 9·0	
[2] C_6H_{14}	0	+ 12	274—345 (c, 0·53—3·27); see Fig. 2.
$CH_3{\cdot}NO_2$	3·78	+ 19·2	
$CH_3{\cdot}OH$	1·64	+ 24·7	189—199 (c, 3·1—14·4) Patterson.[3] 199—197 (c, 3·11—11·8) Patterson.[3]
$CH_3{\cdot}CN$	3·05	+ 35·5[4]	

[1] $c = 3{\cdot}131$.

[2] $c = 0{\cdot}494$.

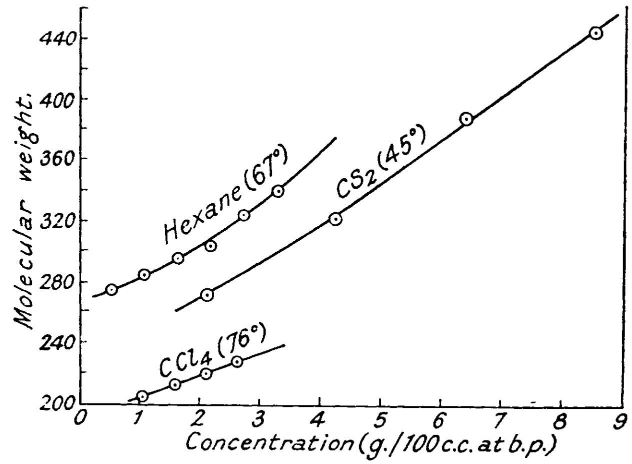
[3] Patterson and Thomson, *Ber.*, 1907, **40**, 1252; Walden, *Ber.*, 1906, **39**, 666.

[4] For methyl tartrate (M, 178) in $CH_3{\cdot}CN$, Walden (*loc. cit.*) finds M, 207—193 for c, 2·52—10·1.

[5] This rotation value was confirmed by measurements extending over the range $c = 1{\cdot}9$—71·2.

FIG. 2.

Molecular weight of ethyl tartrate in solution.



corresponding concentrations. The results are shown in Fig. 2, the range of concentration being limited with carbon tetrachloride by the length of the differential thermometer employed, and with hexane by the low solubility of the ester. In each solvent the ester is comparatively strongly associated even at low concentrations, the extent being greatest in hexane (b. p. 67°) and least in carbon tetrachloride (b. p. 76°). The correction of these values to 20°—at which temperature the optical rotations were determined—would raise them in each case, and in view of the disparity between the boiling points, would probably accentuate the high degree of association in hexane relative to carbon disulphide. It may thus be concluded that the abnormally high rotatory powers recorded for such solutions in Table II (also in the order $C_6H_{14} > CS_2 > CCl_4$) are a direct outcome of the orientation of the solute molecules in the non-polar media. In strong contrast to these molecular-weight values are those found by Patterson (*loc. cit.*) for ethyl tartrate in methyl alcohol and in chloroform. These weakly polar solvents apparently dissociate the ester complexes completely up to moderate concentrations, and the molecular-weight values exhibit little or no variation over a comparatively wide range. The corresponding rotatory powers are therefore characteristic of the *individual* ester molecule in an environment of solvent molecules, a state of affairs which does not hold for hexane, carbon disulphide, or carbon tetrachloride. Incidentally, the molecular-weight values obtained by Patterson for the ester in benzene at 80° range from 213 at $c = \mathbf{1{\cdot}36}$ to 249 at $c = \mathbf{6{\cdot}28}$. The figures thus increase somewhat less rapidly than those in carbon tetrachloride at 76°.

With reference to the change in optical rotation brought about by a rise in temperature, Patterson, Dunn, Buchanan, and Loudon (J., **1932**, 1715) have advanced an empirical generalisation based upon a comprehensive investigation of a large number of tartaric derivatives. They suggest that " in solvents which confer high rotation, the rotation should diminish or else increase slowly with rise of temperature, whereas in solvents of depressing influence the rotation should increase fairly rapidly." In this connexion the theory of dipoles allows a prediction to be made as to *the relative slopes of the temperature–rotation curves for solvents of the two extreme types*, at least in cases where a definite relationship can be traced between the optical influence of the solvent and its polar character.

A rise in temperature may be supposed to affect the rotatory power chiefly—although not solely—by the following two mechanisms. First, the resulting increase of the freedom of rotation around single bonds will modify the configuration or mean resting position of the molecule. Any such modification will proceed with a minimum of disturbance from external sources when the solvent is non-polar, but in the presence of polar solvents the same change may be assumed to occur with such molecules (if any) as are momentarily exempt from the solvent influence. Secondly, when the active compound is dissolved in a polar solvent, a rise in temperature may affect the rotation by altering the extent to which solute and solvent molecules are oriented towards each other (*i.e.*, the extent of solute–solvent association). The latter, in general, diminishes as the mobility of the molecules increases at higher temperatures. In comparison with a solution in a non-polar medium, it therefore follows that the optical displacement due to a polar solvent is more accentuated at low temperatures than at high, with the result that *the temperature–rotation curve for a strongly polar solvent should converge towards that of a non-polar medium as the temperature rises*. For the same reason, the curve for the active compound in the homogeneous condition should exhibit a similar tendency. But since the majority of optically active compounds are less polar than a strongly polar solvent such as nitrobenzene, it may be predicted in general that *in position and direction the temperature–rotation curve for the homogeneous compound will lie between those observed for solvents of the two extreme types*.

These considerations may be illustrated by the following values calculated from data recorded by Patterson (J., 1908, **93**, 1849) for ethyl tartrate in the homogeneous state and dissolved in nitrobenzene and in mesitylene. Thus for a rise of 80° the high values in nitrobenzene solution fall by 20·4°, whereas the relatively low rotations in mesitylene rise by 19·1°. The homogeneous liquid occupies an intermediate position.

$[M]_D$ *for ethyl tartrate.*

t.	Nitrobenzene ($p = 2$).	Homog.	Mesitylene ($p = 10$).
20°	79·1°	16·7°	3·71°
100	58·7	28·0	22·8
Δ 80	− 20·4	+ 11·3	+ 19·1

In so far as Patterson's generalisation cited above implies a convergence of the two types of solvent influence at higher temperatures, it is in agreement with the theoretical deductions. We consider, however, that with non-polar solvents, whether they depress or elevate the rotatory power, the influence of a rise in temperature mainly depends upon the ensuing change in the configuration of the active molecule, and may operate in either direction. Further examples of this temperature relationship will be submitted in the near future.

EXPERIMENTAL.

For purification of solvents, see Part I (J., **1931**, 674.) The ethyl tartrate was obtained from British Drug Houses, Ltd., and was dried and fractionated several times under reduced pressure. It gave $\alpha^{20^\circ}_{5461}$ + 9·51° ($l = 1$); Lowry (J., 1922, **121**, 533) records $\alpha^{20^\circ}_{5461}$ + 56·9° ($l = 6$). Special precautions were taken to prevent access of moisture during subsequent manipulation. In the following tables f_1 denotes the molar fraction of ester as calculated from the weights of solute and solvent.

Rotary Power of Ethyl Tartrate in Solution ($t = 20°$, $l = 4$).

f_1.	c.	α_{5461}.	$[M]_{5461}$.	f_1.	c.	α_{5461}.	$[M]_{5461}$.	f_1.	c.	α_{5461}.	$[M]_{5461}$.
	In mesitylene.				*In toluene.*				*In chlorobenzene.*		
0·050	7·35	+0·08°	+0·56°	0·038	7·184	+1·13°	+8·11°	0·037	7·46	+3·21°	+22·2°
0·1330	19·19	1·48	3·97	0·100	18·31	2·76	7·75	0·209	37·19	10·11	14·01
0·2324	32·72	4·15	6·53	0·1665	30·15	4·53	7·74	0·380	61·55	15·34	12·83
0·3872	52·65	9·06	8·86	0·2373	40·41	6·28	8·01	0·501	79·20	20·23	13·21
0·514	68·20	13·40	10·12	0·3173	50·46	8·26	8·43	0·630	89·86	24·43	14·00
0·689	87·5	20·70	12·18	0·5228	77·15	16·02	10·69	0·791	104·3	30·30	15·01
				0·8050	104·9	28·76	14·12				
	In anisole.				*In benzene.*				*In nitrobenzene.*		
0·028	5·283	+0·31	+3·0	0·0233	5·313	+1·13	10·9	0·031	6·33	10·12	82·3
0·036	6·46	0·78	6·2	0·0722	15·72	3·48	11·4	0·187	34·17	35·27	53·15
0·122	21·79	5·03	11·89	0·1199	22·29	4·98	11·50	0·374	61·09	46·09	38·90
0·225	31·67	8·77	14·26	0·1590	32·26	7·24	11·58	0·562	83·04	47·70	29·58
0·387	50·02	15·88	16·35	0·2140	41·60	9·35	11·57	0·736	99·8	45·66	23·57
0·468	70·18	22·99	16·87	0·2750	49·99	10·92	11·25				
0·633	88·56	27·29	15·87	0·3500	58·68	12·20	10·71				
0·701	94·52	29·09	15·85	0·4284	71·83	15·39	11·03				
0·765	101·8	31·81	16·10								
									In benzonitrile.		
								—	5·094	6·72	67·9
								0·233	40·41	31·52	40·18
								0·466	71·7	42·88	30·80
								0·588	84·5	43·68	26·62

Molecular Weight of Ethyl Tartrate in Solution.—The Menzies–Wright ebullioscopic method (*loc. cit.*) was employed, the following constants being used for 1 mol. of solute in 100 c.c. of solvent at its b. p.: CS_2, 19·4; CCl_4, 32·4; C_6H_{14}, 45·6.

Hexane (24·9 c.c. at 67·2°).			Carbon disulphide (25·9 c.c. at 45·9°).			Carbon tetrachloride (27·0 c.c. at 76·0°).		
w.	Δt.	M.	w.	Δt.	M.	w.	Δt.	M.
0·1335	0·0891°	274	0·5473	0·1510°	271	0·2718	0·1600°	204
0·2671	0·1702	284	1·099	0·2554	322	0·4300	0·2438	212
0·4042	0·2508	295	1·650	0·3174	389	0·5530	0·3026	219
0·5403	0·3267	303	2·205	0·3692	447	0·7078	0·3749	227
0·6789	0·3841	324						
0·8173	0·4400	340						

SUMMARY.

(1) The optical rotation of ethyl tartrate in solution increases in the dextro-sense as the polarity of the solvent rises. Minor irregularities in solvent influence are traced to the incidence of maxima and minima in the rotation–concentration diagrams or to the association of the ester in solution.

(2) On theoretical grounds it is deduced that (*a*) the rotation of the ester in a non-polar medium should increase with the concentration, and (*b*) the temperature–rotation curves for strongly polar and non-polar solvents respectively should converge at higher temperatures, with that for the homogeneous ester assuming an intermediate position and inclination. These conclusions are in agreement with the known behaviour of ethyl tartrate.

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