

The Magneto Rotatory Behaviour of some Optically Active Substances in Solution

By

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Optical rotation has been ascribed to the "structure" of the substance or in Lord Kelvin's phrase to the "chirality" of the medium. Following Larmor's treatment, let us consider the propagation of right handed circularly polarised light in, say, sugar solution, in which its velocity differs slightly from that of a left-handed circularly polarised beam. This gives rise to the phenomenon of rotation of the plane of polarisation. If reflected back it becomes a left-handed train of waves travelling backwards and goes with a different speed, that appropriate to left-handed waves. The medium thus possesses chiral properties, and change of sign of the co-ordinate in the direction of propagation must affect the equations of propagation. Now consider a wave-train travelling in a medium magnetised along X—the direction of propagation, the change of its chirality by reflection no longer produces any change in the velocity. No intrinsic chirality is thus present in the medium and the magnetic rotatory polarisation must be traced to the impressed magnetism which is a vector agency directed along the X-axis and can therefore be connected with difference of velocity for different directions along that axis.

When the reflection is direct, the reflected motion is simply the reversed motion with chirality changed and in a chiral medium the motion is completely reversible, but in the magnetised medium it is not so, and the complete condition of reversion must then involve the reversal of the magnetic field or other extraneous vector agency which causes the rotation by interacting with the material system.

It is interesting to mention Lord Kelvin's¹ ideas here. According to him, an agency which dynamically is to effect the character of the rotational motion of a circularly polarised wave must be of the nature of a moment round the axis rather than a translatory effect along it, *i.e.*, a moment of momentum rather than a linear momentum. This is, except where the medium itself possesses chiral property in which case a linear momentum reacting with it can produce an effect of this kind, though of a second order. Thus if an imposed agency along an axis is to effect a motion round it, the analytical expression of the relation between them must involve screw co-efficients with respect to the medium. An imposed magnetic field must in this way partake dynamically of the nature of rotation round its axis. This together with the fact that magnetic rotation does not exist in free ether, goes far to establish that an impressed magnetic field implies internal rotation in the molecules of the matter with respect to its axis.

In optical rotation the same effect is produced by the internal configuration of the molecules.

It would not be surprising that the two effects are essentially the same, the only difference being that in optical activity the rotation exists due to the internal anisotropy of the molecule, while in the case of magneto-rotation the same effect is undoubtedly produced through external influence.

In this investigation an attempt has been made to find out, if possible, any relationship between the magnetic fields

¹ *Cf. Larmor's "Aether and Matter."*

required to nullify the optical rotation of an active substance dissolved in a solvent with the fields which will be required to produce that same amount of rotation in the pure solvent itself.

During the course of the investigation a paper on the subject was published by G. Calcagni.¹ The original paper could not be available, but from the abstract in the American Chemical Abstracts² it appears that Calcagni tried aqueous solutions of glucose, sucrose, tartaric acid, tannic acid, dl. lactic acid, ammonium hydroxide, eucalyptus oil and castor oil. Calcagni found that the "additional rotation which was produced by the magnetic field was manifest immediately and these increments, the signs of which depended upon the direction of the current were equal, whether positive or negative. The additional rotation was independent of the nature of the substance and its concentrations and values were in all cases 2.0 to 2.5. Moreover with optically inactive substances—water, dl. lactic acid, the additional rotation was the same as that of the active substances. The results in general, indicate that the effect of the magnetic field is exercised on the light which is of an electro-magnetic nature and as in the Zeeman effect, the magnetic field acts on the trajectories of the electrons which produce the light."

The conclusions arrived at by Calcagni, according to the abstract are opposed to the results obtained by W. H. Perkin and his collaborators, who have studied the influence of concentration in magneto-optical rotations in the case of a large number of optically inactive substances. It is not seen why the optical active substances should behave in a different manner altogether. Thus Calcagni's conclusions gave an added interest to this investigation.

¹ G. Calcagni, *Notiz. Chim. Ind.*, **2**, 429, 1927.

² *Chemical Abstracts*, **21**, 8311 (1927).

Experimental.

Two forms of arrangement have been commonly employed for the investigation of substances under magnetic fields. One consists in placing the body between the pole pieces of an electro-magnet. This arrangement was extensively employed by Perkin in his classical experiments. The other arrangement consists in placing an ordinary polarimeter tube inside a large solenoid. This method has been extensively employed in later work, and has also been adopted in the present case.

The latter arrangement has been used in the present work, as with the former it is not possible to employ a sufficient length of liquid column such as is desirable for accurate observation of optical rotations.

The solenoid employed was wound over a "former" of a thin fibre tube. This consisted of 12 layers, each having sixty-two turns of No. 14 S. W. G., D. C. C. copper wire. Each layer was varnished and covered with thin shellac-impregnated paper before the next layer was put on. The fibre tube had an internal diameter of 1.80 cms. and was 0.27 cm. thick. The solenoid was nearly 16 cms. long with an external diameter of about 8 cms.

The current for the solenoid was obtained from the supply mains and was capable of fine adjustment by a sliding rheostat in series with another variable resistance. A Weston precision ammeter, capable of reading to 0.05 amps. was included in the circuit.

As the current was required only for short periods during which the polarimeter settings were made the heating of the coils was not noticeable during the interval.

A Hilger polarimeter with Lippich tripartite field was used. This polarimeter is provided with a V-shaped carrier for placing observation tubes. This had to be removed and

replaced by a suitable board to put the large solenoid. Readings were throughout taken with a sodium flame.

For taking a reading, the polarimeter tube was filled with the solution to be examined and its natural rotation was observed. The magnetic field was then applied so as to produce rotation in the direction opposite to the optical rotation, and carefully adjusted, so as to just nullify the optical rotation of the solution. The current required was noted. Various dilutions of each solution were tried.

It was not found possible to try higher concentrations in several cases as the current required to nullify the optical rotation was found too heavy for satisfactory working due to rapid rise in temperature.

As the solenoid used is air-cored, the magnetic field produced in it varies linearly with the current, so that in place of specifying the field strength the values of current has been given instead.

In the case of solids a concentrated solution was prepared and several dilutions of it were subsequently made. The optical rotations of these were measured and then the current in the solenoid required to just nullify the optical rotation. For liquid-in-liquid mixtures a slightly different method had to be adopted. The optical rotation in these cases was found to be too large and so could not be balanced by current without overheating the solenoid. In these cases, therefore, a constant current of 5 amps. was passed in each case and the rotation produced was measured.

The behaviour of the following substances has been investigated :—

(i) Potassium tartrate, (ii) Rochelle salt, (iii) Ammonium tartrate, and (iv) Dextrose with water as solvent (Fig. 1), (v) Camphor, (vi) Borneol, (vii) Monobromo camphor, and (viii) menthol with ethyl alcohol and benzene as solvents (Fig. 2).

Of the above camphor, borneol and monobromo camphor have also been tried with acetone, toluene and petroleum ether as solvents and camphor, borneol and menthol in ethyl ether also (Fig. 2).

The following optically active mixtures with inactive solvents were also investigated :—

- | | | |
|---------------|---|--|
| Amyl alcohol | { | Benzene.
Petroleum ether.
Acetone.
Toluene. |
| Amyl nitrate. | { | Benzene.
Acetone.
Toluene. |
| Amyl acetate. | { | Acetone.
Toluene.
Petroleum ether. |

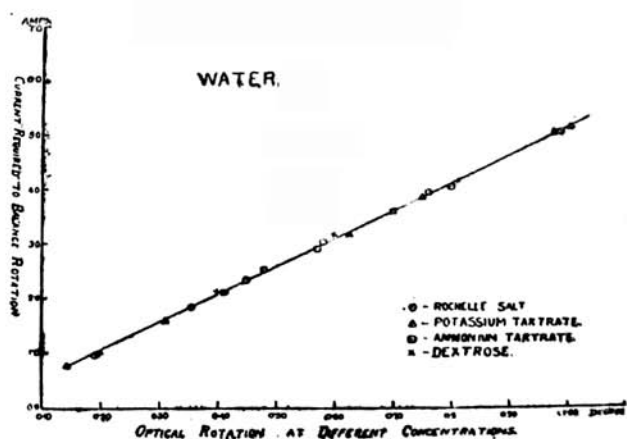


FIG. 1

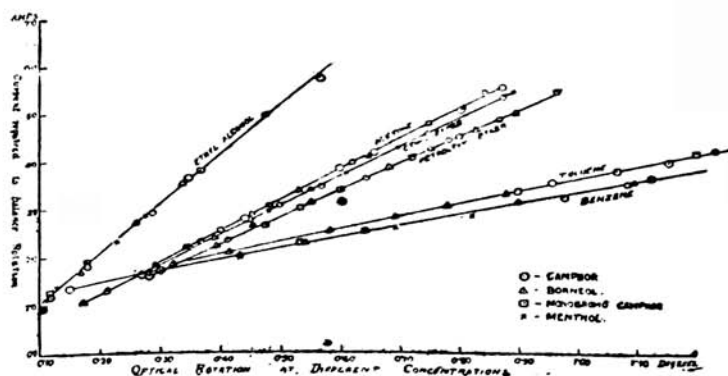


FIG. 2

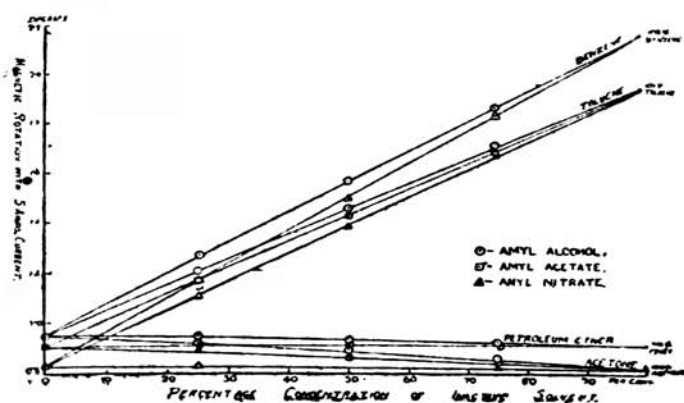


FIG. 3

Results.

The curves in the Figures 1, 2 and 3 illustrate the results obtained. Curves in Figs. 1 and 2 are for solids dissolved in the various solvents while the curves in Fig. 3 are for liquid-in-liquid mixtures.

It would be noticed that in all cases of optically active solutions of solids (Figs. 1 and 2) all the points lie on the same straight line. That is the current required to balance the optical rotation is linearly proportional to the optical rotation. The effect seems to depend only on the

nature of the solvent and within the limits of the experimental conditions, appears to be independent of the nature of the dissolved substance. This point is further evident from Tables I-VII where for 5 amps. current the actual rotations produced in solution and solvent alone are the same.

As solids have only a limited solubility it was found desirable to try solutions in which the concentrations of the dissolved substance could be much increased. Optically active liquids diluted with various inactive liquids were thus investigated. It will be seen from the curves in Fig. 3 (the co-ordinates in these curves are different from the previous curves) that the difference from the case of solids is remarkable. Each of the lines here has got a different slope of its own. This shows that the nature of both the substances plays a part in producing magneto-rotation. This seems to contradict the results arrived at in the case of solids as given above. But the apparent contradiction is undoubtedly due to the fact that for solids the percentage amount of dissolved solid compared to the amount of solvent present is very small. In liquids, however, this concentration is variable between the wide limits of 0 to 100 per cent. and hence the effect produced by the presence of both the active and the inactive molecules of the constituents becomes pronounced. With solids it was obviously too small to be within the capacity of the polarimetric arrangement.

Current = 5 amps.

Field strength = 227 gauss.

Table I. Magneto-Rotation with water only

			0°·99
„	„	„ Rochelle salt solution 2·25%	0°·99
„	„	„ Potassium tartrate solution, 2·21%	0°·99
„	„	„ Ammonium tartrate solution, 1·45%	0°·99
„	„	„ Dextrose solution, 0·96%	0°·99

Table II. Magneto-Rotation with Benzene only	2°·16
" " " monobromo camphor in benzene, 0·99%	2°·16
" " " borneol in benzene, 3·67%	2°·16
" " " menthol in benzene, 2·9%	2°·16
" " " camphor in benzene, 2·4%	2°·16.
Table III. Magneto-Rotation with alcohol only	0°·49
" " " monobromo camphor in alcohol, 0·25%	0°·49
" " " borneol in alcohol, 0·50%	0°·49
" " " menthol in alcohol, 0·35%	0°·49
" " " camphor in alcohol, 0·80%	0°·49
Table IV. Magneto-Rotation with Acetone.	0°·81
" " " Camphor in acetone 1·60%	0°·81
" " " borneol in acetone 1·40%	0°·81
" " " monobromo camphor in acetone, 0·39%	0°·81
Table V. Magneto-Rotation with toluene only	1°·96
" " " camphor in toluene, 2·5%	1°·96
" " " borneol in toluene, 1·43%	1°·96
" " " monobromo camphor in toluene, 0·66%	1°·96
Table VI. Magneto-Rotation with Petroleum ether only	0°·90
" " " camphor in petroleum ether, 1·72%	0°·90
" " " borneol in petroleum ether, 1·53%	0°·90
" " " monobromo camphor in petroleum ether, 0·29%	0°·90
Table VII. Magneto-Rotation with Ethyl ether only.	0°·83
" " " camphor in ethyl ether, 0·85%	0°·83
" " " borneol in ethyl ether, 0·85%	0°·83
" " " menthol in ethyl ether, 0·98%	0°·83

Discussion of Results.

A study of the results obtained brings out the following facts :—

1. That for any particular solvent the current and hence the field required to just balance the optical rotation is

proportional to the optical rotation itself. That is, if I be the current and θ the optical rotation, then

$$I \propto \theta$$

or since the strength of the field H is proportional to I

$$H = K\theta$$

where K is a constant. For optically active solutions of solids the value of K is constant for each solvent.

2. That unlike optical rotation the magnetic rotations of an optically active solution of a substance is independent of the concentration within the range studied.

This result is of considerable interest from the point of view that very small changes in the amounts of optically active substances produce considerable variation in optical rotation. From analogy it was naturally expected that small changes in their concentration should also produce corresponding change in magnetic rotation. Thus, for example, for a solution of menthol in benzene when the concentration changes from 0 to 2.90% the change in optical rotation is from 0° to 2.62° whereas the magnetic rotation remains unaffected.

3. That in the case of solutions of optically active liquids in inactive liquids, where high concentrations of optically active substances could be taken, the magnetic rotation changes with the concentration. It seems to depend upon the volume concentration of each of the liquids. This accords with the conclusions arrived at by Perkin³ and by Schivers.⁴

If θ_1 and θ_2 be the magnetic rotations (for a certain value of magnetising current) for pure (inactive) solvent and the pure (active) solute respectively, then the magnetic rotation (for a particular wave-length) for any intermediate

³ Perkin : Trans. Chem. Soc., 69, p. 1025, 1896.

⁴ Schivers : Compt. Rend., 155, p. 398, 1912.

concentration taken as percentage of the total volume can be expressed as :

$$\delta_n = \theta_1 + \frac{\theta_2 - \theta_1}{100} C_n$$

where C_n is the concentration of the solution in c. c. per cent. for which δ is required.

These results are sharply at variance with the conclusions reached by Calcagni. As given in the abstract referred to before Calcagni's conclusion seems to be that the magneto-rotation is independent of the nature of the intervening media. Our results, on the contrary, are definite that rotation produced is due entirely to the nature of the intervening media. We can interpret our results to say that so far as the influence of an external field is concerned, the optical activity is neither a hindrance nor a help.

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