THE OPTICAL ACTIVITY OF ELECTROLYTES.

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INTRODUCTION.

The difficulties attending the study of the optical activity of electrolytes are considerable. Our conceptions of the nature of electrolytic solutions are still changing: the work of the organic chemist has only served to show the complex nature of the factors governing the phenomenon of optical activity: while the data available are scattered and in many cases incomplete. Over the problem consequently there has been much discussion and disagreement. Yet investigations on the rotatory power of solutions must eventually furnish data which will give some insight into the nature of the solution. It is this consideration which has suggested the research detailed in the present thesis.

A brief account will be given of the advances made in the study of electrolytic solutions, especially during the last ten years. Such a review is necessary if one is to follow and appreciate the work which has been done on the optical activity of electrolytes.

The critical and historical outline of the researches carried out in this field since the time of Biot and Landolt may seem unnecessarily long. So far as the author is aware, however, no summary of this work/

work has been published since Landolt's second edition of the "Optische Drehungsvermögen". As this book appeared some thirty years ago and as a considerable number of papers on this subject have been written in the interval it was judged necessary to give a survey of these papers so that a thorough correlation of the available data could be made.

SOLUTIONS OF ELECTROLYTES.

Our conception of the nature of electrolytic solutions is based on the work of Raoult, who stated in 1882 as the result of his experimental investigations that the boiling-point and freezing-point of a solvent are influenced by the number of molecules of the solute present. Immediately afterwards, Arrhenius advanced his well-known theory of electrolytic dissociation.

At that time much research was being done on the properties of solutions. Grotthus, Clausius, Helmholtz, Kohlrausch, Hittorf and van't Hoff had each made notable contributions towards a solution of the problem. Arrhenius was the first who put forward a comprehensive chemical theory of electrolytes. In his earliest paper presented to the Swedish Academy of Sciences in 1883 the fundamental idea was that the dissolved molecules were of two kinds - active and inactive. The two species were supposed to be in equilibrium, and to obey the Mass Action Law of Guldberg and Waage. The work of Raoult enabled Arrhenius to make the next advance i.e. the active molecules mentioned in his first paper must be charged particles or ions. On this basis Arrhenius constructed his Electrolytic Dissociation Theory.

It/

It had previously been established that chemical equilibrium in the case of gaseous and liquid systems was governed by the Law of Mass Action. Ostwald now applied the principle to the case of electrolytes in solution, where according to the views of Arrhenius there is a chemical equilibrium between the undissociated molecules and the ions. Ostwald derived in this way the well-known Ostwald Dilution Law. It was early noted that strong electrolytes did not obey the law, and many hypotheses have been advanced to account for this anomaly, Arrhenius in his book "Theories of Solution" (1912) suggested various theories to account for this anomaly: one factor mentioned being the electrostatic attractions due to the charges on the ions. To quote Sir James Walker⁽¹⁾ "This factor is now recognised as the chief cause of the abnormality. Arrhenius's original theory is sometimes spoken of as entirely obsolete. But it is well to remember that if the younger men to to-day see a little farther into the nature of electrolytic solutions than Arrhenius. they do so by standing on Arrhenius' shoulders." This is just, and serves as a timely reminder that in considerations of this kind we must recognise the existence not only of an ionic or electrical equilibrium but also of chemical equilibrium as postulated by Arrhenius.

Since the beginning of this century attempts have/

have been made to explain the anomaly by assuming that solutions of electrolytes were almost completely ionised. van Laar, Sutherland, Bjerrum and Milner all suggested that the degree of dissociation of strong electrolytes was much greater than the usually accepted values calculated from conductivity data. To Debye and Hückel⁽²⁾ belongs the honour of deriving a reasonably simple formula, based on the fundamental assumption that the decrease in the molecular conductivity with increase in concentration is due, not to an increase in the concentration of undissociated molecules, but to the decrease in the mobility of the ions. The formula, which also assumes that strong electrolytes are totally dissociated holds moderately well for very dilute solutions. The formula has been modified by Onsager⁽³⁾ to make allowance for the Brownian movement of the ions.

The point of immediate interest is that complete dissociation at the concentrations considered is assumed. Scatchard⁽⁴⁾ summarises the matter thus; "The Debye-Hückel theory does not claim that all electrolytes are completely dissociated or that any specific electrolyte is. It only claims that when there are any ions, there is an electrical force between them. When this force is taken into account it explains the properties of many salt solutions so exactly that we must conclude with Professor Debye that in these cases 'there/

'there are not enough undissociated molecules to show any signs of life.' "

Of the value of the Debye-Hückel-Onsager theory there can be no doubt. In the place of the chemical equilibrium postulated by Arrhenius, prominence is now given to an electrical equilibrium of the charged particles in solution.

When the matter is tested experiment does not always confirm theory. Bjerrum, has come to the conclusion based on an extension of the Debye-Hückel theory, that certain electrolytes, among them potassium nitrate and potassium and sodium iodates cannot be completely ionised. ⁽⁵⁾ Onsager ⁽³⁾ considers that deviations from from the Debye-Hückel equations are due to the presence of measurable concentrations of undissociated molecules. Moreover, the chemist does not find the theory completely satisfying since the conception of a chemical equilibrium enables him to correlate much of his experimental data. ⁽⁶⁾ It is impossible to review all the evidence against the theory of complete ionisation, but three cases may be cited.

Martin ⁽⁷⁾ made exceedingly accurate conductivity measurements of a few uni-univalent salts in very dilute benzonitrile solutions: the concentration of the salts varying between M/500 to M/50,000. At such concentrations the Debye-Hückel theory should hold. Martin assumes the deviations from the theory observed/

observed afford a measure of the degree of dissociation of the salts, i.e. such deviations are due to the presence of undissociated molecules. In this way for each of the salts studied he finds a constant value of the Ostwald Expression: i.e. a chemical equilibrium must be assumed to exist between the ions and the undissociated molecules which is governed by the law of mass action. Put in another way the decrease in conductivity with increase in concentration is due to two factors: the decrease in the mobility of the ions and the increase in the concentration of undissociated molecules.

Again Fajans⁽⁸⁾ has used refractometric evidence to prove the existence of undissociated molecules in solutions of strong electrolytes. It is difficult to give his evidence in a few lines, and it must suffice to state that Fajans regards the changes in molecular refractivity of solutions of electrolytes "as due to the polarisation, or to a deformation of the electron shells of the ions under the influence of the electric fields of neighbouring ions." Fajans sums as follows "From the character and the magnitude of these changes it is concluded that in solutions they must be caused by such oppositely charged ions as are separated from each other by approximately the same distance as in the crystal, i.e. by such ions as are in direct contact with each other with no water molecules/

molecules between them."

The deformation referred to above has been used to account for the changes in rotation of optically active electrolytes. We shall return to this point later.

Very recently J.R. Rao (9) from a study of the Raman effect in solutions of nitric acid found evidence for the presence of undissociated molecules in concentrated solutions. It must be pointed out, however that general conclusions in this matter cannot be reached from the study of solutions of acids, as the hydrogen ion is exceptional in many ways, e.g. it possesses both donor and acceptor properties.

To summarise we may say that evidence points to the fact that while the properties of electrolytic solutions are governed to a greater extent by electrical interionic forces, we must also take into account the presence of undissociated molecules.

This thesis deals particularly with the optical activity of electrolytes, in an endeavour to obtain evidence as to the true nature of electrolytes in solution.

OPTICAL ACTIVITY OF ELECTROLYTES.

Three scientific discoveries of first class importance were made at the beginning of the nineteenth century. In 1808 Malus discovered the phenomenon of polarised light. In 1811 Arago observed that the plane of polarisation was rotated by quartz and Biot followed this up in 1815 by obtaining the same results with solutions of organic substances such as cane sugar. The work of these pioneers has opened up vast fields of research both for the chemist and for the physicist.

Subsequently Biot and other workers undertook a detailed investigation of the optical activity of many organic compounds and great advances were made: the work of Biot, Bouchardat, Gernez, etc. showed that the specific rotations of substances in solution often depend on the temperature and concentration of the solution. Biot further showed that there was a third factor - the nature of the solvent as shown by his experiments on tartaric acid. Biot published these results in 1852⁽¹⁰⁾ and in 1860 he issued a résumé of all his work stressing the factors influencing the rotations of substances in solution⁽¹¹⁾ Nevertheless as late as 1877 Landolt⁽¹²⁾ had to point out that much of the previous work on optical activity was valueless as little or no attention had been paid to the concentration/

concentration of the solutions examined. In this important paper Landolt emphasised the importance of Biot's results, and extended them in the light of the more accurate data obtained by several investigators using improved apparatus.

We shall consider only the work dealing with electrolytes, with special reference to the two factors: -concentration of salt - nature of solvent. The outstanding workers in this field undoubtedly were Biot, Landolt, and Oudemans Jr.

As a result of his researches Biot⁽¹⁰⁾ came to the conclusion that the specific rotation of a solution is not a constant magnitude and that circular polarisation cannot be considered as a result of a simple mechanical distribution of active molecules in an optically indifferent medium. Some of the important factors had been investigated, but prior to 1873 the conditions influencing the optical activity of electrolytes had only been studied to a slight extent. Thus Biot⁽¹³⁾ in 1838 observed that the addition of acids to aqueous solutions of tartaric acid resulted in a diminution of the rotation. In 1863 Hoppé Seyler⁽¹⁴⁾ made a few measurements on the rotations of the derivatives of cholic acid including the sodium and potassium salts. His results however were too meagre to be of much value. In view of the lack of data obtained under definite conditions Landolt⁽¹⁵⁾ in 1873 carried/

carried out a complete investigation of tartaric acids its esters, and its salts. He found that the normal salts all had approximately the same value in 0.5 M solutions.

Molecular Rotations of Metallic Tartrates in 0.5 M Solutions.

Salt	$[\alpha]_D$
Li.Li.	+58.06°
$\text{NH}_4.\text{NH}_4$.	+63.04°
Na.Na.	+59.85°
K.K.	+64.42°
$\text{NH}_4.\text{Na}$.	+61.71°
$\text{NH}_4.\text{K}$.	+63.81°
Na.K.	+62.34°
Mg.	+61.68°

In 1876 Oudemans Jr.⁽¹⁶⁾ undertook a research to find if it were possible to use the optical activity of the cinchona alkaloids as a means of analysing quantitatively mixtures of these substances. In the course of his investigations he examined the rotations of various salts of these alkaloids and the effect of adding excess acid. He did not obtain any regularities, but in 1879⁽¹⁷⁾ in carrying out a similar investigation on the alkaloid quinamine he found that in 1/20 M solution the rotations of the several salts were approximately/

approximately the same.

Rotations of Quinamine Salts in 0.05 M Solutions.

Salt	$[\alpha]_D$	Q = Quinamine
Q.HCl	+114.4°	
Q.HNO ₃	116.5°	
Q.HClO ₃	116.1°	
Q.CH ₃ .COOH	116.2°	
Q.H.CO ₂ H	114.4° 114.9°	
Q. CO ₂ H CO ₂ H	118.1°	
Q.H ₃ PO ₄	117.3°	

His results were thus in harmony with those of Landolt. Oudemans therefore stated the law: "The specific rotation of the alkaloids is modified to the same extent by different acids." Other alkaloids and their salts were investigated and the results confirmed the Oudemans Law. Put more explicitly the law reads: "The rotations of the salts of the monoacidic alkaloids are the same at any given molecular concentration and are not affected by the nature of the acids."

Oudemans⁽¹⁸⁾ in 1886 extended his work by considering the analogous case i.e. the different salts of the same optically active acid (cf. Landolt's work on the tartrates). He found the above generalisation held good for the salts of quinic and podocarpic acids.

All the above work was performed using dilute solutions i.e. $1/40$ M - $1/2$ M. That Oudemans Law holds for dilute solutions and dilute solutions only was shown by Schneider's work on the salts of malic acid.⁽¹⁹⁾

Similar results were obtained from the study of the salts of other optically active acids, e.g. Hartmann's work on the camphorates⁽²⁰⁾ and the recent researches of Darms⁽²¹⁾ on the tartrates.

Rotations of Tartrates in Aqueous Solution.

Salt.	M_D				
	0	0.2	0.5	1.0	1.3
		gm. mol/litre			
Lithium	+42.7°		+39.6°	+38.1°	+36.7°
Sodium	42.7°	42.2°	41.7°	41.0°	40.3°
Ammon.	42.7°	44.6°	44.6°	45.1°	45.3°
Potassium	42.7°	44.7°	45.5°	46.5°	47.0°
Rubidium	42.7°	44.9°	45.8°	47.6°	48.9°

Up to this period there had been no comprehensive theory concerning the nature of electrolytes in solution and therefore the variations of the specific rotations of salts could not be explained, except by using such expressions as "dissociation" and "compound formation" which had then only vague meanings. In 1887 the first volume of the Zeitschrift für physikalische Chemie appeared, thus making the ideas of van't Hoff and Arrhenius available to the scientific world. The/

The value of the Arrhenius theory to account for the variation of the optical activity of electrolytes with concentration was soon recognised. In 1893 Hadrich⁽²²⁾ working in Ostwald's laboratory in Leipzig, used the theory to explain the Oudemans Law. Hadrich reviewed the work of Oudemans and Landolt: prepared a number of optically active strong bases and determined the rotations of their salts at different concentrations. His results were in agreement with those of Oudemans. Meanwhile Kipping and Pope⁽²³⁾ had succeeded in preparing the strong α -Bromocamphor-II.sulphonic acid and had measured the rotations of the acid and its salts. From his own results and from those of Kipping and Pope, Hadrich extended the Oudemans Law. "The rotations of optically active electrolytes tend towards a definite value as the dilution is increased, and this value is independent of the inactive ion." Hadrich further showed that the law was a necessary consequence of the newly advanced dissociation theory. In other words the ionisation theory gave a satisfactory and simple explanation of the Oudemans Law.

Explanation of the Oudemans Law by means of the
Electrolytic Dissociation Theory.

Suppose we have an optically active electrolyte AB in solution. There are three molecular species present - ions A^+ and B^- and undissociated molecules/

molecules AB. The undissociated molecule is optically active and so also is one of the ions, say B^- . In all probability the rotation of the ion B^- will be different from that of the undissociated molecule AB. The specific rotation (or the molecular rotation) of moderately concentrated solutions will therefore depend not only on the concentration of undissociated molecules present, but also on the concentration of the ions B^- . Since at different concentrations there are different proportions of these molecules present, it is to be expected, that at different concentrations the specific rotation of an electrolyte will change. In sufficiently dilute solutions however the quantity of undissociated molecules becomes negligible. Hence in such solutions the specific rotation is dependent entirely on the concentration of ions B^- , and will be independent of the nature of the inactive ion.

A study of the figures obtained by Landolt, Oudemans etc. show that for any series of salts the specific rotations of the salts are not quite constant. This is due in all probability to the fact that at the concentrations considered - sometimes as great as 0.6 M-undissociated molecules are present.

Walden⁽²⁴⁾ set himself the task of finding an optically active acid with a rotation large enough to be measured accurately in extremely dilute solution. He finally selected α -Bromocamphor- Π -sulphonic acid and/

and its salts. As mentioned above this acid had been prepared by Kipping and Pope, who had measured the rotations of its salts. Walden made a much more thorough and accurate investigation, using an exceedingly good polarimeter capable of reading to $1/1000^\circ$ with a tube 4 dm. in length. He also measured the degree of dissociation of the salts at the different concentrations. Now the acid is a strong acid. Hence if the Arrhenius theory were correct, both the acids and its salts should have the same molecular rotation in sufficiently dilute solution. This Walden found to be the case.

**α . Bromocamphor. II. sulphonic acid
and its salts.**

Acid or Salt	V	$[M]_D$	m
Acid	2.08	+ 287°	68.5%
Li	60	269°	94.4%
Na	"	272°	-
K	"	272°	86.8%
Tl	"	269°	87.2%
Ba/2	"	272°	87.3%
Mg/2	"	272°	77.3%
Zn/2	"	270°	-
Ca/2	"	269°	77.2%
	"	271°	74.8%

equivalent.
V = vol. containing 1 gm. ~~molecule~~ of acid or salt.
m = degree of dissociation - calculated from conductivity data.

It will be observed that in spite of the apparent presence of comparatively large quantities of undissociated molecules where we would expect differences in the rotations due to the presence of such different/

different atoms as Lithium and Barium no such differences are to be found. Reference will be made to this point later.

It must be stressed that the Oudemans Law in many cases is only approximately true, i.e. at great dilutions the different salts of (say) an optically active acid have only approximately the same molecular rotation. This point was first brought forward by Shinn⁽²⁵⁾ who repeated and extended Hadrich's work. His results did not agree with those of Hadrich and he concluded that "the rotations of the salts studied (salts of alkaloids) do not tend to become identical for salts containing the same active base." Further Shinn could not bring his results into harmony with the theory of electrolytic dissociation. Stubbs⁽²⁶⁾ has also pointed out that the salts of malic acid do not obey the Oudemans Law.

Salts of Malic Acid.
Mol. Rotation at Infinite Dilution.

Salt	$[M]_0$
K ₂	-15.5°
Na ₂	-16.2°
Li ₂	-19.2°

The molecular rotation at infinite dilution was determined by a graphical method.

The explanation advanced by Stubbs that "at infinite dilution the influence of the metallic ions persists" can scarcely be upheld, else the term infinite/

"infinite dilution" loses its meaning and significance. Some other cause must be sought to account for the departure from the Oudemans Law.

We may call into question some of the figures quoted by Hadrich and Shinn, as these give a false impression of accuracy. For example Shinn admits that his polarimetric readings were not correct to more than 0.04° . As some of the angles of rotation were less than one degree it is obvious that in such cases his accuracy was not very great. Even allowing for this, however, Shinn's conclusions seem to be justified. We can hardly doubt that the variation of the molecular rotation of electrolytes is not always or entirely due to changes in ionisation. The variations of malic acid for instance cannot be due to the changes in ionisation which are comparatively small.

Again Shinn found that the rotations of quinine oleate in chloroform solution underwent changes quite analogous to those of electrolytes in aqueous solution.

Summarising, it may be stated that as a rule the variation of the molecular rotation of electrolytes in solution with change of concentration may be adequately accounted for by means of the Arrhenius Dissociation Theory. (As pointed out above, however, in certain cases ionisation is not the main factor governing such changes of rotation).

on/

On the other hand it seems to the writer that the Debye-Hückel picture furnishes just as complete an "explanation" of the Oudemans Law. Consider as before an optically active electrolyte A^+B^- , the ion B^- being optically active. On the new theory the rotation of the electrolyte is due entirely to the ion B^- , since there are no undissociated molecules in solution. It is obvious that B^- will be more influenced by the surrounding ions in concentrated solutions than in dilute solutions i.e. the nearer A^+ approaches B^- the greater is the influence of A^+ on B^- . Since the ions are electrical systems it is to be expected the electrical system B^- will be altered by the presence of A^+ : in all probability this alteration will also affect the optical properties of the ion B^- . Therefore the rotation of the ion B^- (and consequently of the solution) will depend on the nature of the ionic atmosphere surrounding B^- and will depend on the concentration of the electrolyte in the solution. In very dilute solution the ion B^- will not be appreciably affected by the neighbouring ions, and therefore at such concentrations the rotation will be independent of the nature of the positive ion.

Indeed the complete ionisation theory has certain advantages over the Arrhenius theory. For example Walden's figures (already given) indicate total dissociation of the α -Bromocampher- $\bar{II}$ -sulphonates at concentrations where the Arrhenius theory demands only 60%.

60% - 80% dissociation as measured from conductivity experiments. Noyes⁽²⁷⁾ avoided the difficulty by assuming that in solution there are two types of molecules.

In salts undissociated molecules exist largely as electrical molecules. The molecule is undissociated as shown by conductivity measurements: the optical activity of the molecule is the same as that of the free ion, since the ion exists in the molecule as a "latent ion." Recently Walden⁽²⁸⁾ found that the molecular rotation of the tetra-ethyl ammonium α .bromocamphor- $\bar{I}$.sulphonate is independent of the concentration - at concentrations less than 1 gm.mol/17 litre. Walden maintains that there must be undissociated molecules present and explains the non-variation of the molecular rotation on lines similar to those of Noyes. But is it not simpler to assume that here is evidence of total dissociation at the concentrations considered? In support we may cite the work of Rimbaud⁽²⁹⁾ on the optical activity of rubidium tertrate. In dilute solutions conductivity measurements gave the degree of dissociation as 72.9%. Calculated from the optical activity measurements by using/

using the formula

$$m = \frac{[\alpha] - [\alpha]_0}{[\alpha]_\infty - [\alpha]_0}$$

$[\alpha]$ = sp. rotation of solution examined
 $[\alpha]_0$ = " " at infinite conc.
 $[\alpha]_\infty$ = " " at infinite dilution.

Rimbach found $m = 97.7\%$: a value much more in agreement with the figures now accepted.

Two theories have been advanced to account for the variation of the rotation of an optically active electrolyte with change of concentration. Such changes may be due either to formation of undissociated molecules or simply to the effect of neighbouring ions on the optically active ion. We can test the relative merits of these two theories only after we are more certain of the factors controlling the rotatory power of electrolytes such as change of solvent etc.

An instructive line of research has been the study of the effect produced on the optical activity of electrolytes by the addition of inorganic salts such as sodium chloride, and a résumé of such work may appropriately be given in this place.

That specific salts profoundly alter the rotations of acids, has been known for a long time. In 1837 Biot⁽³⁰⁾ observed that the specific rotation of tartaric acid was greatly increased by the addition of boric acid. Gernez⁽³¹⁾ found that salts of molybdenum had an extraordinarily large effect on the rotations of tartaric acid. Many other results of a like/

like nature were observed. The remarkable effects of such complex electrolytes was accounted for by the assumption that complex additive compounds were formed.⁽³²⁾ Our immediate concern, however, is the effect of the common salts whose influence is much smaller than that of the salts already mentioned.

The earliest investigation of this nature was detailed by Long⁽³³⁾ who added alkali halides to solutions of sodium and potassium tartrates. He found that potassium and ammonium salts raised the rotation while sodium, lithium and thallium salts lowered it. Schutt⁽³⁴⁾ observed the same effect on neutral potassium tartrate with sodium chloride and potassium chloride.

A very complete investigation on the influence of inorganic salts on the rotation of l-malic acid was published by Stubbs⁽³⁵⁾ Stubbs added a great number of different kinds of salts to 1.5 M solutions of the acid and observed the changes in the specific rotations of the solutions. The following table shows the nature and magnitude of the changes observed.

Changes observed on the addition of 1/4 the equivalent weight of salt added to 500 gm. of a 20% solution of

malic acid (1.5 M)

Δ = Change in specific rotation observed.

Salt added	Δ
KI	2.39°
KBr	2.11°
KCl	1.95°
RbCl	1.95°
CsCl	1.94°
NaCl	1.67°
NaNO ₃	1.61°
K ₂ SO ₄	1.48°
NH ₄ Cl	1.16°
Na ₂ SO ₄	1.14°
NH ₄ NO ₃	1.11°
LiCl	0.73°
(NH ₄) ₂ SO ₄	0.65°

Stubbs concluded that electrolytes in general exert a large influence on the rotation of malic acid: further he concluded that this effect is mainly a specific additive property of the radicals or ions..

From the above table and other figures, Stubbs arranged the ions in relation to the change in rotation produced by them.

The alkaline salts have a specially great influence.

Stubbs rejects the theory that the changes are due to compound formation on various grounds among which may be mentioned "the a priori inconceivability of/

Rotation of acid changes from laevo to dextro.

of a salt like KCl forming such complexes." Stubbs also rejects the dehydration theory, "an explanation plausible at first sight that the formation in solution of hydrated molecules by the added salts would act like concentrating the solution, which is well-known to influence the rotation of malic acid in the dextro sense." His evidence is good: for example the salts like lithium chloride, with the greatest affinity for water, exert the smallest influence. The nature of the ionic influence is only vaguely suggested: Stubbs thinks it probable that it is connected with the presence of the hydroxyl group in the acid. This is confirmed by the fact that when the hydroxyl group has been attacked the sensitiveness of malic acid to concentration (and presumably to the addition of salts) disappears.

Patterson and Anderson⁽³⁶⁾ carried out a similar research in 1912 on the effect of adding inorganic salts to solutions of ethyl tartrate.

Effect on the Rotation of a 0.5 M aqueous solution of ethyl tartrate by the addition of various salts (2 M).

Salt	Δ
BaCl ₂	-12.43°
NaI ²	-10.11°
KI	-9.68°
KCNS	-9.09°
Na ⁴	-8.12°
KBr	-7.96°
NaClO	-7.59°
NaNO ₃	-7.31°
KNO ₃	-7.03°
KCl	-6.78°
NaBr	-6.51°
NaCl	-6.05°
NH ₄ NO ₃	-3.87°
NH ₄ Cl	-3.81°
Urea	+0.92°

Δ = Difference in specific rotation observed.

"The results show a very remarkable similarity to those recorded by Stubbs - - - - the resemblance extending even to what might be called the abnormalities." The authors conclude however on several grounds that "it seems improbable that ionisation plays any important part in the matter." As a conclusive piece of evidence they find that salts have similar effects to those quoted above when added to homogeneous ethyl tartrate.

(37)
Bongiovanni in 1912 studied the effects of adding inactive neutral salts to optically active electrolytes. He investigated the following systems:-

Potassium Tartrate	:	Potassium sulphate
Potassium sodium Tartrate	:	Potassium sulphate
Potassium Tartrate	:	Potassium nitrate
quinine Sulphate	:	Potassium sulphate
quinine Hydrochloride	:	Calcium chloride.

He found that though in each mixture the conductivity was markedly less than the sum of the conductivity of the two components, the rotatory power remained the same. It therefore appeared as if the rotatory power were entirely independent of the dissociation of the active substance, i.e. the ions have not a distinct rotatory power of their own.

Recently Darmon⁽²¹⁾ has also investigated the effects obtained by adding inorganic salts to metallic tartrates; his results differ fundamentally from/

from those of Bongiovanni. Darmois considers that the changes of rotation of an electrolyte with change of concentration are due to the same factor causing the changes when an inorganic salt is added to the electrolyte, namely the electric charge of the ions in the solution. He assumes complete dissociation even in concentrated solutions. It was found that on increasing the concentration of the several solutions of the different metallic tartrates, that the rotations of the sodium and lithium salts decreased, while those of the ammonium, potassium, rubidium, and caesium salts increased.

Darmois accounts for these variations by assuming that the decrease of the rotation in the first instance is due to dehydration of the tartrate ion by the cations. The variations of the rotations of the salts are due to the "deformation" (using the word in the sense of Fajans) of the tartrate ions by the charged cations. The work of Fajans shows that in general it is the anions which undergo deformation under the influence of the more compact cations. The deformation produced depends on the radius and charge of the cation. Darmois tests his theory by adding salts containing cations of different "size" and charge to solutions (molecular conc. = 0.25) of sodium tartrate. His results serve to confirm the theory: i.e. sodium and lithium chlorides decrease the rotation, while/

while potassium chloride increases it. Arranged in order of their influence on the rotation Darmsis obtains the following series

Ions of higher charge such as Th^{++++} form what may be termed undissociated molecules: in such molecules the ions exist as latent ions.

As may be expected zinc, cadmium and mercury form complexes.

Darmsis' paper is very interesting and instructive: yet a close reading of the paper reveals many points of weakness. He assumes a vague "dehydration" process to account for some of his results: the evidence of Stubbs and Patterson and Anderson against such an assumption is strong. Again if the series quoted above is indeed an index of the "deformation efficiency" of the cations how is it that in 1.0 molar solutions we have

Salt	$[\alpha]_0$
Potassium Tartrate	+46.5°
Rubidium Tartrate	+47.1°

The rotation of the salts at infinite dilution is +42.7°. It is therefore clear that the rubidium ion in concentrated solutions has a greater effect on the rotation than the potassium ion, just the reverse of what Darmsis' series would lead us to expect.

Before/

Before summarising the papers discussed above there is one point which must be dealt with. The investigations on optically active electrolytes have almost entirely been carried out on the hydroxy derivatives of succinic acid, i.e. malic acid and tartaric acid. It is well known that the presence of a hydroxyl group confers peculiar properties on compounds. Examples of such abnormalities are to be found in the extraordinary variation of rotation of malic acid with concentration and of tartaric acid with temperature. It seems to the author that the choice of tartrates and malates has been unfortunate, and that other substances must be investigated if regularities are to be found.

The considerations which have been advanced are sufficient to show the complex nature of the optical activity of electrolytes, and serve to emphasise the difficulties in the way of arriving at definite conclusions. From the conflicting evidence we may draw the following conclusions.

The changes of rotation of electrolytes with change of concentration and those observed on the addition of inactive salts may be due to the same fundamental cause, namely

1. Changes in the degree of ionisation of the electrolyte.
2. Deformation of the optically active ions by the influence of the ions of opposite charge.

In/

In the cases of malic acid etc. the dominating influence is certainly not ionic in nature: there must be other factors such as complex formation due to the residual affinity of groups such as the hydroxyl.

The changes of rotation of electrolytes produced by the addition of inactive electrolytes cannot be accounted for by the dehydration theory.

It is evident from the above considerations that the study of the optical activity of electrolytes in solution has been confined to a great extent to investigations on the hydroxy derivatives of succinic acid. It is the purpose of this communication to investigate with a fair degree of accuracy the optical activity of electrolytes of quite a different type namely those containing no group such as the hydroxyl or amino. From a somewhat limited selection ammonium- α -bromocamphor- Π -sulphonate was finally chosen, not only because it fulfills the above requirements, but also because its rotation in aqueous solution is sufficiently great to allow measurements to be made in very dilute solutions.

Moreover it is from studies of salts of this type that Walden and Noyes have based their conclusions with regard to the degree of ionisation of strong electrolytes.

This electrolyte has been studied from the point of view of the variation of rotation produced by change of concentration and by the addition of various optically inactive electrolytes and non-electrolytes. Other salts of α -bromocamphor- Π -sulphonic/

sulphonic acid might have been investigated, but the acid is extremely difficult to prepare in the pure state.

It was originally intended to investigate the optical activity of other electrolytes: after a few preliminary experiments however it was decided to make a thorough study of the variations in the rotation of the above mentioned ammonium salt, which though small were definite.

It was hoped that the results would give some information concerning the nature of solutions of electrolytes.

EXPERIMENTAL.

In carrying out this research nearly all the solutions investigated contained the same concentration of the active ammonium salt. - molecular concentration 0.1. In order that the rotations might be strictly comparable it was necessary that there should always be the same quantity of ammonium salt between the end plates of the polarimeter tube. Careful attention was therefore given to the weights, volumes, and temperature of the solutions.

(In order to determine the weight of water in each solution density observations were made.

All volume and density measurements were determined at 20.0°C.

Apparatus.Standard Flasks.

All the flasks were calibrated in a thermostat maintained at 20.0°C. They were all found to contain 50.06 c.c.

Pyknometers.

These were of the usual Ostwald type and were calibrated for use at 20.0°C. Except in the case of solutions containing volatile liquids such as methyl alcohol, the end caps were dispensed with. The capacity of the pyknometers was approximately 5 c.c. All densities were referred to water at 20.0°C.

Polarimeter.

The polarimeter was a Hilger instrument provided with a Lippich three shadow polarizer and two verniers reading to 0.01° . It was fitted with direct vision spectroscopic attachments for reading rotations with the three mercury lines (yellow, green and violet). The tube was 4 dm. in length and was provided with a central cup, moveable end caps, and a water jacket through which water was pumped from a thermostat by means of an electrically driven water turbine (Schmidt and Haensch). The temperature of the water in the thermostat was so regulated that the solution in the polarimeter tube was maintained at 20.0°C ($\pm 0.2^\circ$) as measured by a small thermometer placed in the central cup.

A quartz mercury vapour lamp working at atmospheric pressure was used as source of light for the mercury green line.

Chemicals.

The chemicals were for the most part Analytical Reagents. Each reagent was tested for gross impurities by the standard methods and where necessary were purified. In cases of doubt the reagents were analysed. For example potassium oxalate was titrated against standard potassium permanganate solution : the percentage of water in magnesium sulphate was determined, etc.

In/

In almost all cases salts were recrystallised from water, and organic liquids distilled in order to obtain them absolutely pure as the slightest opalescence of the solutions made the polarimetric readings less reliable. The chemicals were thoroughly dried and kept in desiccators.

The ammonium-a-bromocamphor-II-sulphonate was obtained from the British Drug Houses, Ltd., and was recrystallised from hot water till the rotation was constant: $[M]_{5461}^{20} = +347.2^{\circ}$: molar conc. of solution = 0.1 cf. the figures of Pope and Read⁽³⁸⁾ $[M]_{5461}^{22} = +346.6^{\circ}$: molar conc. = 0.2 (approx.).

Mode of operation.

The ammonium salt and the optically inactive substance to be added were carefully weighed (in the cases of acetic acid, etc. definite volumes were run in from standard solutions in a burette). The standard flasks were freed from grease and the salts then poured in through a filter funnel. In order that this might be carried out readily the salts were always ground in a mortar. Distilled water was added and the flask shaken till the salts dissolved completely. Water was then added so that the level was a little below the standard mark, the flask was immersed up to the mark in a thermostat at 20.0°C , and allowed to remain there for 15 minutes. A few drops of water were added from a small pipette till the standard volume/

volume was reached. After shaking the solution was ready for use.

Before filling, the polarimeter tube was always thoroughly cleaned with water, washed with alcohol, and dried by a blast of air. The plates were fixed lightly on the ends of the tube, and a zero reading taken. (Control experiments showed that it was unnecessary to fill the tube with water before obtaining a zero reading- a procedure recommended in many practical text books.)

The solution was poured into the tube, and the water from a thermostat passed through the water jacket till the temperature of the solution reached 20.0°C. The polarimeter readings were easily obtained, half-a-dozen usually being sufficient for each solution. All readings were made with the mercury green line -
 $\lambda = 5461.$

Finally the densities of the solutions were taken at 20.0°C, observing the usual precautions.

Accuracy of the Results.

Repeated experiments showed that the readings were accurate to 0.02°, except in the case of a few solutions such as those containing methyl alcohol. The following table shows the accuracy attained, using several different solutions.

Rotations of Ammonium- α -Bromocampher-II-Sulphonate 0.02 M.

Solution	α_{5461}^{20}
1.	+2.75
2.	+2.75
3.	+2.74
4.	+2.75
5.	+2.73
6.	+2.74

As most of the angles measured were approximately $+13^\circ$, an accuracy of 1 in 500 can legitimately be claimed. Little difficulty was experienced in obtaining weight and volume measurements with this degree of accuracy.

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RESULTS.Rotations of ammonium.α bromocamphor.Ⅱ. sulphonate in
Aqueous Solutions.

All volumetric and density determinations were made
at 20.0°C.

$$D_{20}^{20} = \frac{\text{wt. of vol. of soln. at } 20^{\circ}\text{C.}}{\text{wt. of vol. of water at } 20^{\circ}\text{C.}}$$

Knowing the density of a given solution and
the weights of the salts in it, it is possible to
calculate the weight of water in the solution.

Wt of solutions = 50.06 c.c.

The mercury green line was used in all the
polarimetric observations.

Table 1.Ammonium.α .Bromocamphor.Ⅱ. Sulphonate

Mol.wt. of ammon. salt = 328.13

Weight of salt means weight of anhydrous salt.

Variation of Molecular Rotation with Concentration.

Molar conc. of ammon. salt.	Wt. of ammon. salt. gm.	D_{20}^{20}	Wt. of water. gm.	α	$[M]$	Error in $[M]$
0.02	0.3285	1.003	49.71	+ 2.76	+345°	±2°
0.04	0.6568	1.005	49.81	+ 5.52	+345°	± 1.5°
0.10	1.654	1.013	48.94	+13.84	+346.1°	± 0.3°
0.20	3.285	1.026	47.92	+27.97	+349.6°	± 0.3°
0.30	4.924	1.039	46.94	+42.44	+353.5°	± 0.3°

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Table 2.Ammon. α . Bromosamphor. II. Sulphonate.Rotations in presence of KCl - molar conc. = 1.0

Wt. of KCl = 3.732 gm.

Δ = Difference between the molecular rotation of the amm. salt in a solution containing KCl and the molecular rotation in aqueous solution.

Δ' = Difference between the weight of water in an aqueous solution of the ammonium salt and the weight of water in a solution of the ammonium salt containing KCl.

Molar Conc. of Ammon. Salt	Weight of Ammon. Salt	D_{20}^{20}	Weight of Water	α	[M]	Error in [M]	Δ	Δ'
	gm.		gm.					gm.
0.02	0.3285			+2.78°	+347.9°	$\pm 2.0^\circ$	2.9°	
0.04	0.6569	1.051	48.08	+5.68°	+348.7°	$\pm 1.5^\circ$	3.7°	1.43
0.10	1.643	1.058	47.46	+14.00°	+349.8°	$\pm 0.3^\circ$	3.7°	1.48
0.20	3.285	1.071	46.48	+28.31°	+353.4°	$\pm 0.3^\circ$	3.8°	1.44
0.30	4.924	1.084	45.48	+42.90°	+357.5°	$\pm 0.3^\circ$	3.7°	1.46

ROTATIONS OF AMMONIUM. α . BROMOCAMPHOR. II. SULPHONATE. MOLAR CONC. = 0.1

In presence of Acids.

Wt. of ammon. Salt. = 1.643 gm.

Table 3. Hydrochloric Acid.

Molar Concentration of acid.		Wt. of acid.	D_{20}^{20}	Wt. of water.	α	[M]
		gm.		gm.		
-		-	1.013	48.94	+13.89°	+347.2°
0.5	0.5	0.913	1.022	48.46	+13.90°	+347.5°
1.0	0.5	1.826	1.030	47.94	+13.90°	+347.5°
1.5	1.5	2.739	1.039	47.49	+13.90°	+347.5°
2.0	2.0	3.652	1.049	47.07	+13.90°	+347.5°
2.5	2.5	4.565	1.055	46.48	+13.84°	+345.9°
3.0	3.0	5.478	1.066	46.07	+13.83°	+345.7°
3.5	3.5	6.391	1.072	45.49	+13.77°	+344.2°
3.89	3.89	7.198 gm	1.079	45.21	+13.73°	+343.2°
10 (approx)		18 (approx)	-	-	+12.65°	+316.1°

Table 4. Acetic Acid.

-	-	1.013	48.94	+13.89°	+347.2°
0.5	1.501	1.018	47.68	+13.89°	+347.2°
0.75	2.252	1.021	47.09	+14.05°	+351.1°
1.0	3.002	1.022	46.38	+14.08°	+351.1°
2.0	6.010	1.030	43.78	+14.26°	+357.2°
3.0	9.015	1.038	41.15	+14.42°	+360.5°

Table 5.Monochloroacetic Acid.

Molar Concentration M of Acid	Wt. of acid	D_{20}^{20}	Wt. of water	α	$[\eta]$
	gm.		gm.		
-	-	1.013	48.95	+13.88°	+346.9°
1.0	4.728	1.047	45.89	+14.19°	+354.6°
2.0	9.456	1.079	42.77	+14.56°	+363.9°
2.7	12.77	1.103	40.61	+14.75°	+368.6°

Table 6.Dichloroacetic Acid.

0.268	1.727	1.029	48.00	+13.98°	+349.4°
0.525	3.393	1.042	47.98	+14.11°	+352.6°

Table 7.Trichloroacetic Acid.

0.335	2.739	1.040	47.54	+13.99°	+349.7°
0.5	4.089	1.053	46.84	+14.10°	+352.4°
2.28	18.66	1.185	38.87	+15.30°	+383.3°
2.5	20.45	1.202	37.92	+15.46°	+386.4°

ROTATIONS OF AMMONIUM. α . BROMOCAMPHOR. II. SULPHONATE, MOLAR CONC. = 0.1In presence of inorganic salts.Table 9. Lithium Chloride.

Molar conc. of LiCl.	Weight of LiCl. (gm.)	D_{20}^{20}	Weight of Water. (gm.)	α	[M]
-	-	1.013	48.95	+13.89°	+347.2°
0.5	1.061	1.025	48.47	+13.93°	+348.1°
0.75	1.692	1.031	48.23	+13.93°	+348.1°
1.0	2.122	1.037	47.98	+13.96°	+348.2°
1.5	3.182	1.049	47.51	+13.92°	+347.8°
2.0	4.244	1.060	47.02	+13.91°	+347.6°
2.5	5.306	1.072	46.56	+13.86°	+346.5°
3.42	7.276	1.090	45.50	+13.81°	+345.3°

Table 10. Ammonium Chloride.

0.5	1.339	1.021	48.02	+13.91°	+347.6°
0.75	2.009	1.026	47.57	+13.93°	+348.1°
1.0	2.678	1.030	47.09	+13.94°	+348.3°
1.5	4.107 ^{0.17}	1.037	46.11	+13.96°	+348.9°

Table 11. Ammonium Sulphate.

0.125	0.827	1.023	48.60	+13.95°	+348.6°
0.25	1.654	1.031	48.17	+13.99°	+349.7°
0.375	2.479	1.041	47.86	+14.00°	+349.9°
0.5	3.309	1.048	47.37	+14.02°	+350.3°

Table 12.

Sodium Chloride.

Molar conc. of Salt.	Weight of Salt.	D_{20}^{20}	Weight of Water	α	$[M]$
-	gm. -	1.013	gm. 48.96	+13.89°	+347.2°
0.2	0.5850	1.022	48.79	+13.91°	+347.6°
0.5	1.463	1.033	48.46	+13.95°	+348.6°
1.0	2.926	1.053	48.00	+13.97°	+349.2°
2.0	5.850	1.092	47.02	+13.97°	+349.2°
3.0	8.778	1.126	45.85	+13.96°	+348.9°

Table 13. Sodium Iodide.

0.6	3.751	1.071	48.08	+14.00°	+349.9°
1.0	7.506	1.127	47.09	+14.06°	+351.4°
1.5	11.86	1.184	46.22	+14.10°	+352.4°
2.0	15.01	1.241	45.29	+14.08°	+351.8°
2.5	18.76	1.297	44.36	+14.03°	+350.5°
2.7	20.22	1.318	43.94	+14.04°	+350.9°
3.0	22.512	1.350	43.24	+13.19°	+349.7°

Table 14. Sodium Sulphate.

0.125 375	0.8891	1.029	48.84	+13.93°	+348.1°
0.25 75	1.778	1.044	48.70	+13.98°	+349.4°
0.5 15	3.553	1.074	48.42	+14.01°	+350.1°
0.75 225	5.335	1.104	48.28	+14.10°	+352.4°
0.875 268	6.219	1.117	47.85	+14.15°	+353.6°
1.0 30	7.110	1.132 1.127	47.77	+14.17°	+354.10°
1.125 3375	8.000	1.146	47.58	+14.19°	+354.6°

Table 15.Potassium Fluoride.

Molar Conc. of Salt.	Weight of Salt	α	[M]
	gm.		
-	-	+13.89°	+347.2°
0.48	1.410	+13.97°	+349.2°
1.0	2.908	+14.00°	+349.9°
1.94	5.645	+14.06°	+351.4°
2.98	8.668	+14.13°	+353.1°

Care must be taken when using potassium fluoride solutions that there is no hydrofluoric acid present: it was found that freshly prepared solutions did not attack glass.

Table 17.Potassium Bromide.

Molar conc. of Salt.	Weight of Salt.	D_{20}^{20}	Weight of Water	α	[M]
	gm.		gm.		
0.5	2.978	1.054	47.99	+13.97°	+349.2°
1.0	5.957	1.097	47.18	+13.98°	+349.5°
1.5	8.936	1.139	46.27	+14.05°	+351.1°
2.0	11.711	1.176	45.37	+14.07°	+351.6°
2.5	14.89	1.220	44.37	+14.06°	+351.4°
2.95	17.25	1.251	43.55	+14.05°	+351.2°

Table 16.Potassium Chloride.

Molar conc. of Salt.	Weight of Salt. (gm.)	D_{20}^{20}	Weight of Water (gm.)	α	[M]
	gm.		gm.		
0.5	1.865	1.036	48.21	+13.97°	+349.2°
1.0	3.731	1.059	47.49	+14.00°	+349.9°
1.5	5.600	1.081	46.72	+14.05°	+351.1°
2.0	7.464	1.102	45.90	+14.08°	+351.8°
3.0	11.194	1.145	44.32	+14.07°	+351.6°
3.5	13.061	1.166	43.52	+14.08°	+351.8°

Table 18.Potassium Iodide.

0.5	4.153	1.071	47.67	+14.03°	+350.5°
1.0	8.312	1.129	46.40	+14.08°	+351.8°
2.0	16.62	1.246	43.93	+14.16°	+353.8°
2.5	20.77	1.303	42.62	+14.12°	+353.9°
3.0	24.94	1.359	41.26	+14.09°	+352.1°

Table 19.Potassium Sulphate.

Molar conc. of Salt.	Weight of Salt	D_{20}^{20}	Weight of Water	α	[M]
	gm.		gm.		
-	-	1.013	48.95	+13.89°	+347.2°
0.25 ⁷⁵	2.150	1.047	48.44	+13.97°	+349.2°
0.375	3.270	1.064	48.20	+14.01°	+350.1°
0.5 ¹⁵	4.358	1.080	47.92	+14.07°	+351.6°

Table 20.Potassium Oxalate.

0.25 ⁷⁵	2.080	1.042	48.30	+14.01°	+350.1°
0.5 ¹⁵	4.160	1.072	47.82	+14.07°	+351.6°
1.0 ³⁰	8.320	1.127	46.28	+14.26°	+356.3°
1.375	11.30	1.153	44.61	+14.36°	+358.8°

Table 21.Magnesium Sulphate.

0.25 ¹⁰	1.507	1.042	48.87	+13.94°	+348.3°
0.375 ¹⁵	2.260	1.057	48.87	+13.98°	+349.4°
0.46 ¹⁸⁴	2.792	1.067	48.83	+14.02°	+350.3°

Table 22.Cadmium Chloride.

Molar conc. of Salt.	Weight of Salt	D_{20}^{20}	Weight of Water	α	$[M]$
-	gm.		gm.		
-	-	1.013	48.95	+13.89°	+347.2°
0.5	4.588	1.091	48.23	+13.94°	+348.3°
1.0	9.178	1.169	47.55	+13.98°	+349.4°
1.25	11.47	1.206	47.09	+14.04°	+350.9°
1.5	13.76	1.244	46.60	+14.09°	+352.1°

Table 23.Cadmium Iodide.

0.125 ¹¹ 375	2.291	1.051	48.47	+13.96°	+348.9°
0.25 75	4.582	1.088	48.09	+14.07°	+351.6°
0.5 15	9.159	1.162	47.22	+14.29°	+357.2°
0.75 2.25	13.731	1.237	46.38	+14.52°	+362.9°
1.0 3.0	18.32	1.312	45.53	+14.80°	+369.9°

Table 24.Cadmium Sulphate.

0.25 1.0	2.608	1.063	48.82	+13.94°	+348.3°
0.5 2.0	5.217	1.111	48.60	+13.98°	+349.4°
0.75 3.0	7.824	1.160	48.45	+14.05°	+351.1°

Table 25.

Mercuric Cyanide.

Molar conc. of Salt.	Weight of Salt	D_{20}^{20}	Weight of Water	α	[M]
	gm.		gm.		
-	-	1.013	48.95	+13.89°	+347.2°
0.05	0.633	1.023	48.79	+13.87°	+346.7°
0.125	1.581	1.037	48.55	+13.81°	+345.3°
0.25	3.161	1.062	48.22	+13.76°	+343.9°

Table 26.

Potassium Cyanide.

Molar conc. of Salt.	Weight of Salt.	α	[M]
0.5	1.632	+13.64°	+340.9°
1.0	3.267	+13.57°	+339.1°

Table 27. Potassium Ferrocyanide.

0.125	2.303	+14.05°	+351.1°
0.25	4.606	+14.13°	+353.1°

Table 28. Barium Chloride.

0.50	5.212	+13.91°	+347.6°
0.75 M	7.818	+13.95°	+348.6°

ROTATIONS OF AMM. α . BROMOCAMPHOR. II. SULPHONATE. MOL. CONC. = 0.1.

In presence of Non-Electrolytes.

Table 29.

Methyl Alcohol.

Molar conc. of Methyl Alcohol	Weight of CH ₃ OH	D ₂₀ ²⁰	Weight of Water	α	[M]
-	gm. -	1.013	gm. 48.94	+13.89°	+347.2°
0.5	0.8024	1.011	48.18	+13.89°	+347.2°
1.0	1.6039	1.007	47.02	+13.89°	+347.2°
2.0	3.208	1.002	45.17	+13.91°	+347.6°
3.0	4.806	0.9972	43.33	+13.93°	+348.1°
4.0	6.410	0.9917	41.46	+13.98°	+349.4°

Table 30.

Urea.

-	-	1.013	48.94	+13.89°	+347.2°
0.5	1.503	1.021	47.82	+13.93°	+348.1°
1.0	3.007	1.030	46.76	+13.94°	+348.3°
1.5	4.509	1.037	45.62	+13.97°	+349.2°
2.0	6.013	1.044	44.46	+13.98°	+349.4°
2.5	7.513	1.052	43.36	+14.02°	+350.3°
3.0	9.016	1.060	42.20	+14.07°	+351.6°

Table 31.

Glycerol.

0.5	2.303	1.024	47.17	+13.96°	+348.9°
1.0	4.606	1.035	45.41	+14.05°	+351.1°
2.0	9.222	1.055	41.81	+14.20°	+355.1°
3.0	13.83	1.077	38.29	+14.38°	+359.3°
4.0	18.44	1.098	34.73	+14.56°	+363.9°
Pure Glycerol as Solvent		1.269	-	+16.62°	+415.4°

DISCUSSION OF RESULTS.Variation of Molecular Rotation of Electrolytes with
Change of Concentration.

In the case of amm. α .bromocamphor. $\overline{\text{II}}$. sulphonate a small but definite increase in the molecular rotation with increase in the concentration was observed.

Molar conc. or Amm. Salt	$[\alpha]_{5461}^{20}$
0.02	+345°
0.04	+345°
0.10	+347.2°
0.20	+349.6°
0.30	+353.6°

These changes are very similar to those observed by Darmois⁽²¹⁾ in the case of several tartrates. For comparison the figures for ammonium tartrate are given below.

Molar conc. or Amm. Salt.	$[\alpha]_D$
0.087	+43.8°
0.20	+44.1°
0.50	+44.6°
0.65	+44.8°
1.00	+45.1°

It appears that below molar concentrations of 0.1 there is little or no variation in the molecular rotation of such salts. This is in agreement with Walden's values for the tetra.ethyl.ammonium salt of α .bromocamphor. $\overline{\text{II}}$.sulphonic acid - $\text{C}_{10}\text{H}_{14}\text{BrOSO}_3^- \text{N}(\text{Et})_4^+$ in/

in aqueous solution, and with the figures quoted by him⁽²⁸⁾ for several tartrates.

Molecular Concentration of the Salt.	$[M]_D$
0.05	+274°
0.01	+271°
0.005	+269°
0.003	+277°

cf. The molecular rotation at infinite dilution of the α -bromocampher. II. sulphonates determined by Walden⁽²⁴⁾ in an earlier communication $[M] = +270^\circ$.

Tartrates.

Salt.	Molecular Conc. of Salt.	$[M]_D^{20}$
Disodium	0.03	+60.2°
Sodium	0.1	+62.5°
Potassium	0.2	+62.5°
Rubidium	infin. dilution	+62.2°
	0.05	+62.3°

It appears that in many cases solutions whose concentrations are less than 0.1 M exhibit no change in rotation with dilution. If this result be general it may be inferred that in dilute solutions (i.e. less than 0.1 M) there is complete dissociation.

A statement by G. N. Lewis⁽³⁹⁾ on the additive properties of electrolytic solutions may be commented on at this point. "Indeed in all strong electrolytes the partial volume, heat capacity, internal energy, viscosity, refractive index, rotatory power - in fact practically all the significant physical properties of the undissociated part of the electrolyte - seem practically identical with the properties of the constituent ions. If we had no other criterion for the degree of dissociation, these facts would undoubtedly lead us to regard salts up to a concentration of normal or half normal as completely dissociated." So far as results from the study of the optical activity of electrolytes furnish us with information as to the dissociation of electrolytes, this statement by Lewis does not hold for solutions whose concentrations are greater than 0.1 M. As pointed out in the Introduction the changes in rotation at higher concentrations may be adequately explained either by change in the degree of dissociation of the electrolyte, or by the deforming influence of the positive ion on the optically active negative ion.

Rotations of Amm. α . Bromocamphor. II. Sulphonate.

In presence of optically inactive electrolytes and
non-electrolytes.

The effect of adding a fixed weight of potassium chloride to solutions of the ammonium salt was first investigated.

Rotations of Ammonium Salt in presence of Potassium
Chloride.

Molar Concentration of KCl = 1.0.

Δ = Increase in the molecular rotation of the ammonium salt in a solution containing KCl, 1.0 M and the molecular rotation in aqueous solution.

Molar Conc. of Ammon. Salt	$[M]_{5461}^{20}$	Δ
0.02	+347.9 °	2.9 °
0.04	348.7 °	3.7 °
0.10	349.8 °	3.7 °
0.20	353.4 °	3.8 °
0.30	357.5 °	3.7 °

It is evident that the increase in the molecular rotation of the ammonium salt caused by the addition of a definite weight of potassium chloride is independent of the concentration of the ammonium salt. This is in harmony with the conclusion of Stubbs⁽³⁵⁾ in regard to the effect of adding salts to l-malic acid, "that the influence of the salt on the specific rotation depends mainly on the concentration of the solution with regard to that salt, and not on the concentration of the malic acid present."

Finally an extensive investigation into the influence of different types of electrolytes and non-electrolytes on the rotations of 0.1 M solutions of Ammn. α -bromocamphor. II. sulphate was made.

If Darms' view be correct it is to be expected that the addition of inorganic salts to the salt of an optically active acid would result in changes of the molecular rotation of the electrolyte; and further that the following regularities would be observed. The magnitude of the change of rotation would be (1) inversely proportional to the size of the added cation; (2) proportional to the change of the added cation (3) dependent on the concentration of the added salt. As already pointed out (p.27) Darms' theory is open to objections when subjected to experimental tests. In order to investigate the matter/

matter further, many salts of different types were added to solutions of amm. α . bromocamphor. $\overline{\text{II}}$. sulphate. In addition the effects of acids of different strengths, and non-electrolytes such as alcohol were observed. The changes in rotation produced in this way may be seen in the following table.

amm. α . Bromocamphor. $\overline{\text{II}}$. Sulphonate. Molar conc. 0.1
Effect on the rotation produced by the addition of
various salts etc.

The molar concentration of the added substance in all cases was 0.5

Δ = Increase in $[\text{M}]_{5461}^{20}$ caused by addition of inactive compound. The Probable experimental error = $\pm 0.6^\circ$

Added Compound.	Δ
CH_3COOH	0.0°
HCl	0.3°
CH_3OH	0.3°
NH_4Cl	0.4°
BaCl_2	0.4°
LiCl	0.9°
Urea	0.9°
CdCl_2	1.1°
NaCl	1.4°
KBr	1.4°
Glycerol	1.7°
KF	2.0°
KCl	2.0°
CdSO_4	2.2°
NaI	2.7°
Na_2SO_4	2.9°
$(\text{NH}_4)_2\text{SO}_4$	3.1°
$\text{CH}_2\text{Cl.COOH}$	3.4°
KI	3.4°
MgSO_4	3.4°
K_2SO_4	4.2°
K_2CrO_4	4.2°
CHCl_2COOH	5.2°
CCl_3COOH	5.2°
CdI_2	10.0°
$\text{K}_4\text{Fe}(\text{CN})_6$	12.0°

In three cases a decrease in the rotation was observed.

Molar concentration of added substance = 0.25.

Added Compound	Δ
Hg(CN) ₂	-4.3°
KCN	-4.3°
AgNO ₃	-17.5° (approx.)

The above tables serve to show that.

1. The change produced by the addition of each of these substances is small compared with those observed by Darms. For example this author found that the specific rotation of a 0.25 M solution of sodium tartrate was decreased from +42.5° to +23.0° by a 0.6 M solution of BaCl₂. The greatest change observed in the case of the amm. α -bromocamphor-11-sulphonate was in the case of potassium ferrocyanide i.e. the molecular rotation increased from +347.2° to +359.2°. The changes in many cases were so small that only by great care and by using a very good polarimeter were differences in the rotation possible to detect.

2. The magnitude of the change of rotation cannot be correlated with the charge or size of the ions. This is shown more clearly by the two tables given

Chlorides.

Salt Molar conc. = 0.5	Δ
HCl	0.3°
NH ₄ Cl	0.4°
BaCl ₂	0.4°
LiCl	0.9°
CdCl ₂	1.1°
NaCl	1.4°
KCl	2.0°

Potassium Salts.

Salt Molar conc. = 0.5	Δ
KBr	1.4°
KF	2.0°
KCl	2.0°
KI	3.4°
K ₂ SO ₄	4.2°
K ₂ C ₂ O ₄	4.2°

To find out whether the effect on the rotation can be regarded as the sum of two terms - the change in the rotation due to the cation and that due to the anion - the following figures were tabulated.

Δ has the same significance as before.

Salt	Δ	Diff.	Salt	Δ	Diff.	Salt	Δ	Diff.	Salt	Δ	Diff.
NH ₄ Cl	0.4°		KCl	1.4°		NaCl	1.4°				
		1.6°			0.6°			1.1°			
NH ₄ Br	2.0°		KBr	2.0°		NaBr	2.5°				
		0.7°			1.4°			0.2°			
NH ₄ I	2.7°		KI	3.4°		NaI	2.7°				
		0.2°			1.2°			0.2°			
(NH ₄) ₂ SO ₄	2.9°		K ₂ SO ₄	4.2°		Na ₂ SO ₄	2.9°				
NH ₄ Cl	0.4°		NH ₄ Br	2.0°		NH ₄ I	2.7°		(NH ₄) ₂ SO ₄	2.1°	
		1.0°			0.5°			0.0°			-0.2°
NaCl	1.4°		NaBr	2.5°		NaI	2.7°		Na ₂ SO ₄	2.9°	
		0.0°			-0.5°			0.7°			+1.3°
KCl	1.4°		KBr	2.0°		KI	3.4°		K ₂ SO ₄	4.2°	

The accuracy of the figures quoted is $\pm 0.6^\circ$. It is just possible that the effect of these salts is additive: to test this point still more accurate measurements would be necessary. If the effect is indeed/

indeed ionic it would seem probable that it is the anion and not the cation which has the dominating influence. This is contrary to Darms' theory. There must, however, be some other effect since weak electrolytes like monochloroacetic acid and non-electrolytes like glycerol have greater effects on the rotation than many of the salts mentioned above.

3. Non-electrolytes such as glycerol have an appreciable influence on the rotation of the salt.

It is manifest therefore that in the case of amm. α . bromocamphor. II. sulphonate no regularities were obtained such as those observed by Stubbs and by Darms in the case of *l*. malic acid and the salts of tartaric acid respectively.

On the Arrhenius Theory a 0.1 M solution of a uni-univalent salt is 80% - 90% dissociated and the addition of an excess of another salt should result in a considerable decrease in the ionisation. The exact determination of this decrease in the ionisation is difficult since the laws governing the ionic dissociation of mixtures of strong electrolytes are not completely understood. The equilibrium expression for a mixture of two electrolytes with a common ion has been obtained and experimentally confirmed by Arrhenius (40.) but when the case of two salts without a common ion is considered the conditions of equilibrium are more difficult to work out. The expressions which have

been obtained are derived from the isohydric principle which in turn is based on the law of mass action. As strong electrolytes do not obey this law, such expressions are largely of an empiric nature and must be accepted with reserve. In many cases, however, especially in dilute solutions, the equations derived from the isohydric principle are found to be of service. Two quantitative results may be cited.

Arrhenius⁽⁴⁰⁾ found "that in a mixture of two salts with a common ion each salt has a degree of ionisation equal to that which it has when alone present in a solution in which its ions have a concentration equivalent to that of the common ion in the mixture." If then an ammonium salt is added to a 0.1 N solution of ammonium. α . bromocampher. $\overline{\text{II}}$. sulphonate so that the total ammonium ion concentration is 0.6 N, the degree of dissociation of the second salt may be expected to diminish from 85% to 77%. If the changes of rotation observed on the addition of an optically inactive salt are indeed due to the change in the ionisation of the optically active salt, this decrease in ionisation should be accompanied by a considerable change in the rotation. This was not found to be the case.

Molecular Rotation of Amm. α .bromocamphor. $\overline{\text{II}}$.sulphonate. 0.1 N.In presence of ammonium salts. 0.5 N.

Amm. salt.	+347.2°
In presence of 0.5 NH_4Cl	347.6°
In presence of 0.5 $(\text{NH}_4)_2\text{SO}_4$	349.7°

Moreover the addition of larger concentrations of ammonium salts was only found to influence the rotation of the amm. α .bromocamphor. $\overline{\text{II}}$.sulphonate to a slight extent. (See graphs.)

When the salts in a mixture have no common ion the equilibrium seems to be conditioned by the "total ion concentration", i.e. the sum of the concentrations of all the positive or negative ions.

^{41.} Sherril for example found that in a mixture of NaCl and K_2SO_4

the equilibrium is governed by $[\text{Na}^+] + [\text{K}^+]$

Consider now the case of a 0.1 N solution of amm. α .bromocamphor. $\overline{\text{II}}$.sulphonate, to which has been added excess of another salt (say 0.5 N). Since this second salt is present in considerable excess, it may be assumed that the ionisation of the ammonium salt is changed to a much greater extent than that of the added salt, and consequently that the total ion concentration of the solution will depend to a large extent on the concentration and degree of ionisation of the added salt. If the total ion concentration be the/

the main factor governing the ionisation of the ammonium salt, it is obvious that the addition of excess of different salts of the same equivalent concentration but of different degrees of ionisation should result in decreasing the ionisation (and at the same time changing the rotation) of the ammonium salt to varying degrees. Now it is well known that the ionisation of salts is determined to a large extent by the salt type - uni.univalent, uni-divalent etc. For example.

Degree of Dissociation of 0.5 N solutions of several Electrolytes.

Determined by conductivity measurements.

Salt	Degree of Dissociation.
KCl	78%
BaCl ₂	67%
MgSO ₄	38%

Hence the addition of equivalent quantities of these salts should influence the changes in the ionisation and the rotation of the ammonium. α . bromo-camphor. $\bar{\text{II}}$.sulphonate to different extents. Only small changes in the rotation however were found.

Molecular Rotation of Amm. α . Bromocamphor. $\bar{\text{II}}$.sulphonate 0.1N

In presence of salts of different types. 0.5 N.

Salt added	[M]
-	+347.2°
KCl	+349.2°
BaCl ₂	+347.6°
MgSO ₄	+348.3°

Indeed salts in general seem to have only a very/

very small effect on the rotation of the ammonium salt - (see tables and graphs). It seems therefore impossible to correlate the comparatively large changes in the ionisation with the extremely small variations in the optical activity.

The above method of treating solutions of electrolytes is open to criticism and indeed the possibility of examining quantitatively equilibria between ions and undissociated molecules has been questioned⁽⁴²⁾. Moreover the determination of the ionic concentrations present in solution is attended by great difficulties since it is now established that the conductivity ratio $\frac{\lambda_c}{\lambda_\infty}$ does not yield an accurate measurement of the degree of dissociation of an electrolyte. In view of such difficulties the problem of electrolytic solutions has been attacked from the thermodynamic standpoint. The thermodynamic method in the hands of G.N. Lewis, Brønsted and others has proved very fruitful, and it is of interest to review the results of the present research in the light of their conclusions.

Whereas the older theory involved an equilibrium between molecular species of two types, the modern theory does not concern itself with the nature of the molecules in solution, but deals with the departure of the solutions in question from obeying the laws of ideal solutions. From a study of the free energy changes Lewis defined what he termed the activity of/

of an electrolyte or ion, and from this activity he derived a new term - the activity or thermodynamic degree of dissociation.

$$\text{Activity coefficient of Electrolyte} = \frac{\text{Mean Activity of the Ions}}{\text{Molality of the Electrolyte}}$$

The activity coefficient thus affords a measure of the fraction of the concentration of the electrolyte which is active from the chemical point of view.

In formulae therefore molar concentrations are not now used: instead the activities, or the product of molar concentrations and the thermodynamic degree of dissociation are substituted. The question may therefore be asked - is there any relationship between the effect of added salts on the optical activity of an electrolyte and the activities of such salts?

It has already been pointed out that the degree of dissociation as determined by $\frac{\lambda_c}{\lambda_\infty}$ is conditioned by the type of electrolyte. Lewis and Randall⁽⁴³⁾ showed that the same holds for ^{the} thermodynamic degree of dissociation.

For example⁽⁴⁴⁾

Activity Coefficients of Typical
Molality = 0.1 Electrolytes.

KCl	0.794
BaCl ₂	0.501
MgSO ₄	0.166

As shown above these salts have practically the same effect on the rotation of the optically active ammonium salt. The thermodynamic activities of the salts/

salts and their effects on the optical activity of the ammonium. α .bromocamphor. II. sulphonate do not therefore seem to be related.

Finally reference must be made to a concept introduced by Lewis and Randall⁽⁴⁵⁾ - the ionic strength of a solution. The ionic strength of a solution of electrolytes is defined as half the sum of the molality of each ion multiplied by the square of the valence. The study of electrolytic solutions has shown the prime importance not only of the concentration of the ions, but also of their charges. To quote Lewis and Randall "there is unquestionably a factor depending upon the concentration of the ions and upon their charge, which largely determines the properties of any electrolytic solution ----- this factor is the ionic strength." It would seem however that the influence of electrolytes on the optical activity of a salt is not conditioned by the ionic strength of the solution: solutions containing different types of electrolytes of the same molar concentration and consequently having different ionic strengths are found to have altered the rotation to the same extent: while on the other hand salts of the same type giving rise to solutions of the same ionic strength affect the rotation of the ammonium salt to different extents.

u = ionic strength.

Salt	u	Δ	Salt	u	Δ
NH_4Cl	0.5	0.4°	NH_4Cl	0.5	0.4°
BaCl_2	1.5	0.4°	NaCl	0.5	1.4°
NaI	0.5	2.7°	KI	0.5	3.4°
Na_2SO_4	1.5	2.9°			

It is scarcely surprising however that the variation of the rotation of the ammonium salt and the ionic strength of the solution are not related since in moderately concentrated solutions of salts the specific properties of the ions must be taken into consideration.

The effect of adding great excess of inactive substances was investigated, and the results are shown in the accompanying graphs. The difficulties attending a correlation of the variation of rotation with the known properties of the added compounds are apparent.

It is of course possible that the structure of the camphor molecule renders the asymmetric carbon atoms less sensitive to changes in ionisation or to the influence of the cation. This possibility has been suggested by Walden⁽²⁸⁾ but is not very plausible, since the magnitude of the change of rotation of the amm. α -bromocamphor- II -sulphonate with concentration is comparable to that observed in the case of (say) ammonium tartrate, so that the camphor structure does not seem to exert any noticeable "protective influence" on/

on the asymmetric carbon atoms.

It was suggested that the changes in rotation might be connected with the weight of water in the solutions i.e. by adding a salt to a solution of the active ammonium salt there might be a "concentration effect". Thomsen⁽⁴⁸⁾ observed in his studies on the rotations of tartaric acid in the presence of such and acids as citric, /acetic, that the foreign body introduced with-draws water in some unknown way, and concentrates the solution of the active acid.

For example a solution containing

50 gm. water

30 gm. tartaric acid

20 gm. citric acid

possessed the rotation of a 50% aqueous solution of tartaric acid, i.e. each acid appropriated water in the proportion in which each was present. Thomsen's theory has been criticised, but it seemed worth while to discover whether the salts etc. which were added had any "concentration effect" on the active ammonium salt. The weight of water in each solution was determined and it was obvious that no simple relationship existed. See for example the table given overleaf.

Ammonium α -bromocamphor-11-sulphonate.

Δ has the same meaning as before.

δ is the difference between the weight of water contained in 50.06 c.c. of a 0.1 M solution of the ammonium salt and the weight of water contained in 50.06 c.c. of a 0.1 M solution of the ammonium salt containing the added compound (molar concentration 0.5). If we consider the concentration of the ammonium salt as

$$\frac{\text{weight of amm. salt in solution}}{\text{weight of water in solution}}$$

then δ is a measure of the concentration effect of the added substance,

Compound added 0.5 M	Δ	δ
Urea	0.9	gm. 1.13
KCl	2.0	0.74
Na ₂ SO ₄	2.9	0.53
MgSO ₄	3.4	0.09
COCl ₂ .COOH	10.0	2.11

We must conclude that the changes in rotation observed are due to some factor not ionic in nature. It is possible for example that the ammonium salt is not really a single substance but is an equilibrium mixture of two isomers. Kipping⁽⁴⁶⁾ showed that the α -bromocamphor-11-sulphonic acid can exist in two forms - a cis and a trans configuration:-

With regard to the ammonium salt Kipping states that it "certainly appears to be homogeneous as its optical properties do not change when it is repeatedly recrystallised. Whether this is due to the impossibility of separating the salts of the normal form from that of the iso, or to the complete transformation of the iso salt into the normal form during the preparation is uncertain: the author inclines to the first view." If the ammonium salt does not indeed consist of two dynamic isomers - Kipping suggests that there is about 5% of the iso form present - it is quite possible that the addition of salts alters the equilibrium.

Thus Clough⁽⁴⁷⁾ in the case of the tartrates considers that "inasmuch as the equilibrium is conditioned by solvent, concentration, and temperature, change of rotation is also dependent on these factors ---. It is evident that the presence of certain inorganic salts in aqueous solution profoundly alters the equilibrium of the two iso dynamic forms." It is therefore tentatively suggested that the changes of rotation observed in such cases as the tartrates and amm. α -bromocamphor-II. sulphonate when inorganic salts are added, are due essentially to a change in the equilibrium between two dynamic isomers, each of which possesses a different rotation.

So little work has been published on the effect of adding salts to optically active electrolytes that/

that it is impossible to draw conclusions without a certain amount of reserve. Moreover it is difficult to correlate many of the results. On the one hand the rotation of a salt like sodium tartrate is influenced to a great extent by the addition of optically inactive salts, while at the other extreme ammonium- α -bromocamphor- $\overline{\text{II}}$ -sulphonate is only slightly affected. It seems feasible that the large changes observed in the case of the salts of the hydroxy acids are due to the presence of the -OH group, and that electrolytes containing no groups possessing residual affinity (other than the -SO₃H or COOH group) do not exhibit great changes in rotation.

SUMMARY.

1.

A survey of the work done on the optical activity of electrolytes and the writer's own results show that great uncertainty still exists concerning the factors governing the rotatory power of electrolytes.

2.

The change in the molecular rotation of aqueous solutions of ammonium. α . bromocamphor. $\overline{\text{II}}$. sulphonate have been studied.

Little or no variations were observed in solutions whose molar concentrations were less than 0.1.

The changes observed at higher concentrations may be accounted for by assuming either changes in the degree of dissociation of the electrolyte or a deforming influence of the positive ion on the optically active negative ion.

3.

The effect of adding optically inactive electrolytes and non-electrolytes to 0.1 M aqueous solutions of ammonium. α . bromocamphor. $\overline{\text{II}}$. sulphonate has been investigated.

The changes in rotation were small.

The variations are practically independent of the concentration of the active ammonium salt, but depend on the concentration of the substance added.

SUMMARY CONTD.

The results are not in harmony with the original Dissociation Theory of Arrhenius, nor the "Deformation Theory" of Darrois.

The effect of the various electrolytes on the rotation does not depend on their thermodynamic activity.

4.

The possible relationship between the variations in rotation and the chemical configuration of the ammonium. α .bromocamphor. $\overline{\text{II}}$.sulphonate ion is discussed.

In conclusion the author has great pleasure in thanking Sir James Walker for his encouragement and valuable guidance throughout the research.

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