CHAPTER VII

ROTATOMETRIC DETERMINATION OF ACID DISSOCIATION CONSTANTS OF THE LIGANDS DBSC AND NBSC AND FORMATION CONSTANTS OF THEIR METAL CHELATES
Molecules without a plane of symmetry are optically active and capable of rotating the plane of polarization of light. Although such activity is common in organic molecules, it is not a 'wonder' in the realm of inorganic chemistry particularly after an outstanding work of Werner and others. Metal chelates may occur as 'enantiomorphs' due to asymmetry around the central metal ion, though the ligand may not be optically active. This optical isomerism is observed in 'inert' complexes where the optical isomers can actually be separated by available methods. But such separation may not be possible if the complex is labile. When the ligand itself contains asymmetric centres, various diastereoisomers are formed, not necessarily in statistically expected proportions. But instead certain forms are distinctly favoured, depending on the configuration and conformation of the ligands and relative amounts of steric hindrance resulting in the various diastereoisomers. The formation of least unsymmetrical asymmetric isomer is generally favoured. However, more recently, the changes in optical rotation of optically active ligands when they form complexes, have been ascribed simply to environmental effects, due to co-ordination process.

An excellent study on the effect of added acid and base on the optical activity of amino acids has been made by Wood. More recently Ghosh and co-workers studied the effect of variation of pH, and the presence of metal ions [Cu(II), Hg(II), Zn(II), and Cd(II)] on the optical activity of the ligand N-benzensulphonyl-L-glutamic acid. Rotametric methods have been used to determine the dissociation constants of a number of acids and bases.
In the present investigation, two optically active ligands DBSC and NBSC have been selected for study. The ligand DBSC contains two and NBSC contains one asymmetric centres respectively (Table-I). The changes in optical rotation of these ligands during the course of their neutralisation with alkali and formation of complexes with some metal ions have been utilised for the determination of their acid dissociation constants and also the formation constants of some of their metal chelates.

Experimental Procedure

A plot of observed optical rotation maintaining the total concentration of the optically active ligand constant throughout as a function of pH of the solution has been termed a "Rotatometric titration" by Pacsok and Juvet. The plots are extremely useful for the determination of pH range in which various optically active species exist. Rotatometric titration of an optically active ligand in absence of a metal ion may be utilised for the determination of their acid dissociation constants. For this purpose optical rotations of a number of solutions of the ligand, each containing the same amount of the ligand, maintained at different pH values, are determined and plotted against pH. For the determination of formation constants of metal chelates, optical rotations of a number of solution containing definite amount of the ligand and metal ion, adjusted to different pH values are plotted against pH of the solution as well as against negative logarithm of free ligand concentration. The molar rotation (\(\alpha D\)) values of various species may be evaluated by graphical extrapolation from inflections of such plots, with due correction for excess ligands (r) where necessary and may be refined by successive approximation.
In the present work all the solutions were made in (1:1) aqueous-dioxane and ionic strength of each solution was maintained constant (μ = 0.60) throughout employing requisite amount of NaClO₄. All experiments were conducted at room temperature 30 ± 0.5°C. Measurement of pH values of the solutions were made with Cambridge Portable-Type pH-Meter calibrated with standard aqueous buffer solutions, viz., standard 0.01M HClO₄, sodium hydrogen phthalate and borax buffer, with due temperature corrections. Optical rotations due to sodium light were recorded with the help of a photoelectric polarimeter using a 0.25 dm tube.

Preparations and standardisations of the reagents have already been discussed in the case of potentiometric study.
The changes in optical rotation of the ligand DBSC (RH⁺) during the course of its neutralisation with alkali and complex formation with Cu²⁺ ions have been utilised for the determination of its practical acid dissociation constants (k² and k⁻) and the formation constant of its Cu(II) complex Cu(RH₂). The rotatometric titration of DBSC in presence of Cu²⁺ ions could not be completed due to intense blue colouration of the solution at moderate pH values. Such titrations of DBSC in presence of Zn²⁺ and Cd²⁺ ions indicate no complex formation at lower pH values, as the rotatometric titration curves for these titrations follow the same path as the curve obtained in the absence of these ions. This indicates that Zn²⁺ and Cd²⁺ ions have no influence on the optical rotation of the ligand DBSC, in other words there is no complex formation between the ligand and these metal ions at these pH values. At comparatively higher pH values of the solution, optical rotation of DBSC has showed an increase due to the presence of Zn²⁺ and Cd²⁺ ions. But the titrations could not be completed due to the commencement of precipitation of oxides at higher pH values of the solutions. From the nature of the curves (Fig.82) it is apparent that stability of the DBSC chelates are in the order Cu(II) > Zn(II) > Cd(II).

Procedure:

A standard 10.89×10⁻⁸M solution of DBSC was prepared by dissolving 13.890 g of recrystallised DBSC in purified dioxane and making the volume upto 250 ml. Preparation and standardisation of Cu(ClO₄)₂, Zn(ClO₄)₂, Cd(ClO₄)₂, NaClO₄, HClO₄ and NaOH solution have been described in Chapters IV and VI. Aliquots of 4.50 ml
of this solution along with 8.0 ml of purified dioxane were placed in a number of 25 ml measuring flasks. For the determination of dissociation constants of the ligand, increasing amount of NaOH solution and requisite amount of NaClO₄ solution and water were added to each flask so as to get solutions of different pH values at a constant ionic strength (μ = 0.50) when volumes were made up to the mark with (1:1) aqueous dioxane as there were contractions in volumes. The solutions were each 19.23x10⁻⁶ M with respect to DBSC in (1:1) aqueous-dioxane. For the determination of formation constants of metal chelates, in addition to 4.50 ml of 10.62x10⁻⁶ M DBSC solution and 8.0 ml of dioxane, an amount of M²⁺ ions (M = Cu, Zn and Cd) were placed in each flask so that metal ligand ratio become 1:1, different volumes of NaOH solution, requisite amount of NaClO₄ solution and water were added and volumes were made up to the mark as stated earlier. Each solution thus contained metal:ligand in the ratio 1:1 in (1:1) aqueous-dioxane at a constant ionic strength (μ = 0.50). The solutions were allowed to equilibrate. pH values of each solution were measured and their optical rotations for sodium light were recorded. Data are stated in Tables 30 and 32. The observed rotations were plotted against pH (Fig.32).

Acid dissociation constants (k₁ and k₂) of DBSC:

Optical rotation of DBSC (BH₄⁻) has showed a decrease with increase of pH of the solution (Fig.32) upto pH = 6.50, after which rotation remained constant without showing any change on further increase of pH of the solution. This constancy of rotation with increase of pH indicates the end point of the rototometric titration. The fall in rotation with increase of pH of the DBSC solution must be due to the appearance of some new species in the solution and should be due to BH₄⁻ and RH⁺, formed as a result of stepwise acid dissociation of BH₄⁻ as represented by the reactions (31) and (32) for which the primary and secondary dissociation constants are given by (33) and (34) respectively.
EXPERIMENTAL POINTS

- DBSC
- DBSC + Cu(II)
- DBSC + Zn(II)
- DBSC + Cd(II)

CALCULATED CURVE USING ROTATOMETRIC

$pk_2^* = 4.04$, $pk_1^* = 4.68$
Optical rotation is an additive property. Optical rotation of a solution is the sum of rotations due to all the active species present in the solution. Thus at any stage of the titration of DBSC after attainment of the equilibrium the observed rotation $\alpha$ is given by

$$\alpha = \frac{R_A}{40} \sum \mathcal{M}_{D} + \frac{R_B}{40} \sum \mathcal{M}_{D} + \frac{R_C}{40} \sum \mathcal{M}_{D} \quad \ldots \quad (98)$$

where $\sum \mathcal{M}_{D}$, $\sum \mathcal{M}_{D}$, and $\sum \mathcal{M}_{D}$ are the molar rotations of the species $\text{RH}_A^+$, $\text{RH}_B^-$, and $\text{RH}_C^-$ respectively and $R_A$, $R_B$, and $R_C$ are their equilibrium concentrations.

The molar rotation values have been calculated from the relation

$$\frac{\alpha}{1} = \frac{40 \alpha}{1} \quad \ldots \quad (99)$$

where $\alpha$ is the observed rotation of $'m'$ molar solution of the optically active substance in tube of $'l'$ dm in length. Thus for a 0.25 dm tube

$$\frac{\alpha}{1} = \frac{40 \alpha}{1} \quad \ldots \quad (100)$$

Thus if $'a'$, $'b'$ and $'c'$ be the observed rotations of $'R'$ molar solutions of $\text{RH}_A^+$, $\text{RH}_B^-$ and $\text{RH}_C^-$ respectively, where $R$ is the total concentration of the ligand, one may get from equations (35), (98) and (100)

$$\alpha = \frac{aR_A + bR_B + cR_C}{R_A + R_B + R_C} \quad \ldots \quad (101)$$

From the plot of $\frac{\alpha}{(\text{obs.})}$ against pH (Fig.32) the value of $'c'$ can be easily extrapolated, but those of $'a'$ and $'b'$ could not be accurately determined - evidently due to overlapping of steps (31) and (32). Now from equations (35), (34) and (35) one may obtain
and from equations (33), (34), (35) and (101)

\[
\frac{(c_R - c)}{k_2} = a \frac{(H^+)^{1/2}}{k_1} + b \frac{H^+}{k_1^2} \quad \cdots \cdots (103)
\]

Now with the help of linear plot of \( \frac{(c_R - c)}{k_2} \) against \( \frac{H^+}{k_1^2} \), the values of 'a' and 'b' have been obtained from the slope and intercept of the straight line, taking the values of \( k_2 \) and \( k_1 \) as obtained potentiometrically under identical conditions.

Considering the latter stages of the titration, when \( R_2 \) is negligibly small, one may get from (103)

\[
\frac{(c_R - c)}{k_2} = b \frac{H^+}{k_1}
\]

or

\[
\log \left( \frac{(c_R - c)}{k_2} \right) = \left( pk_1 - \phi \right) + \log b \quad \cdots \cdots (104)
\]

The value of 'b' has also been found out from the intercept of the linear plot of \( \log \left( \frac{(c_R - c)}{k_2} \right) \) against \( \left( pk_1 - \phi \right) \) using equation (104).

With the values of 'a', 'b' and 'c', at hand, one may now re-evaluate \( k_2 \) and \( k_1 \) from the linear plot (Fig.33) of the equation

\[
\frac{(c - c)}{k_2} + \frac{\phi - \phi}{k_1} = \frac{1}{k_2} (c - c) + \frac{1}{k_2} \frac{\phi - \phi}{k_1} \quad \cdots \cdots (105)
\]

which may be deduced from equations (33), (34), (35) and (101). The values of 'a', 'b', \( k_2 \) and \( k_1 \) have been refined by successive approximation. Results are stated in Table-31.
Limits of error have been determined by comparing the experimental plot of \( \alpha_{\text{obs.}} \) against pH with the calculated one obtained on plotting \( \alpha_{\text{calc.}} \) against pH. \( \alpha_{\text{calc.}} \) have been obtained from the relation

\[
\alpha_{\text{calc.}} = \frac{\frac{[H^+]^2}{k_{12}^1} + b \cdot \frac{[H^+]^1}{k_{12}^1} + \frac{c}{k_{12}^1}}{\frac{[H^+]^2}{k_{12}^1} + \frac{[H^+]^1}{k_{12}^1} + 1}
\]

employing the refined values of 'a', 'b', \( k_{12}^1 \) and the experimental value of 'c'. Standard deviations ( ) have been calculated from the relation

\[
\sigma = \sqrt{\frac{\sum (\alpha_{\text{expt.}} - \alpha_{\text{calc.}})^2}{\text{Number of observations}}} \quad \ldots \ldots \quad (107)
\]

Data are stated in Table-30. Molar rotations (\( \sum \frac{M}{D} \)) values of the species \( \text{RH}_4^+, \text{RH}_5^-, \text{RH}_6^{2-} \) have been calculated from equation (100) using the refined values of 'a', 'b' and the experimental value of 'c'. Results are stated in Table-31.

**Formation constant (K) of the complex \( \text{Cu(RH}_6^2 \) :**

A sharp rise in the optical rotation with increase of pH has been observed in the rotostometric titration of DBSG in presence of \( \text{Cu}^{2+} \) ions (Fig.52). This sharp increase in rotation should be due to the appearance of some new species in the solution with increase in pH values. Evidently DBSC undergoes complex formation with \( \text{Cu}^{2+} \) with the formation of the active species \( \text{Cu(RH}_6^2 \) according to the reaction represented by (61) (where \( \text{M} = \text{Cu(II)} \)), which occurs together with the stepwise acid dissociation (31) and (32) of DBSG with increase of pH of the
solution. The formation constant ($K$) of the complex $\text{Cu(RHg)}$ is given by equation (52).

Now if the concentrations of the species $\text{Cu(RH)}$ and $\text{Cu(R)}^{2-}$ which may arise as a result of stepwise acid dissociation of $\text{Cu(RHg)}$ as represented by (59) and (60) be assumed negligible at the early stages of complex formation, then after attainment of equilibrium the relations (53) and (54) will hold good and if $\alpha$ be the observed rotation, then

$$\alpha = \frac{aR + bR + cR + dM}{R + R + R + M}$$

where 'd' is the observed rotation of a 'R' molar solution of $\text{Cu(RHg)}$ under the experimental condition. The significance of the other notations have been stated earlier.

Molar rotation $\mathcal{M}_{\text{RHg}}$ of the species $\text{Cu(RHg)}$ is given by the relation

$$\mathcal{M}_{\text{RHg}} F = \frac{404d}{K}$$

(109)

The value of $K$ may be obtained from the intercept of the linear plot of $R_g$ against $\frac{M(d - \alpha)}{B}$, using the equation

$$\frac{M(d - \alpha)}{B} = R_g + \frac{1}{K}$$

(110)

where $B = \mathcal{C}(\alpha - a)$. The equation (110) can be deduced on solving equations (33), (54), (55), (56), (57) and (108). The value of $R_g$ may be obtained from equation...
But as the value of *d* could not be obtained from the rotametric titration curve (Fig. 33), it is not possible to find out *R₂* from equation (111) and hence *K* from graphical solution of equation (110).

An approximate value of *R₂* may be obtained employing the potentiometrically determined value of *K* as follows.

On solving equations (33), (34), (52), (53) and (54) one may obtain

$$R = \frac{B}{1 + K R_2} \left( \frac{(d-a) \left( B_i^0 + B_i^0 + 1 \right) + \frac{M B R_2}{1 + K R_2}}{C_0} \right)$$

which can be arranged as a quadratic equation in *R₂*, such that

$$R_2 = \frac{1}{2} \left[ \frac{4K R_2 (B - K) A}{A} \right] \pm \left( \frac{4K R_2 (B - K) A}{A} \right)^{\frac{1}{2}}$$

where

$$A = \frac{B_i^0}{k_i^0} + \frac{B_i^0}{k_i^0} + 1.$$
which can be obtained from equation (110). The refined value of $R_g$ has now been obtained from equation (111) using the rotatometric values of $k^*_2$, $k^*_1$ and the value of 'd' evaluated from graphical solution of the equation (114). The value of 'd' and 'R_g' have been refined by successive approximation. Finally the value of $K$ has been obtained from the intercept of the plot of $\frac{4d-2M}{B}$ against refined value of $R_g$ (Fig.35), using the equation (110). The value of $K$ has been refined by successive approximation and the refined value of $\log K$ has been stated in Table-33, which also contains the molar rotation ($\zeta_{M_J_D}$) of the species Cu(III) obtained from equation (109) using the refined value of 'd'.

The standard deviation ($\sigma$) has been calculated by employing equation (107), for which $\alpha_{(calc.)}$ values have been obtained from the equation

$$
\alpha_{(calc.)} = \frac{R_g}{K} \left[ a \frac{C_{B}^2}{k_{12}^2} + b \frac{C_{B}^2}{k_{1}^2} + c + d \frac{M_{K}}{1 + E_{R_2}} \right] \quad \ldots \quad (116)
$$

which may be deduced from equations (35), (34), (53), (53), (54) and (108). Data are stated in Table-32.
Fig. 33

\[ 2x \left( \frac{c-x}{a-x} \right) \times 10^8 \]

\[ 2x \left( \frac{x-b}{a-b} \right) \times 10^3 \]

Fig. 33
Fig. 34.
Table-50. Rotatometric titration of DBSC (RH₄) at 30 ± .5°
DBSC = 19.23x10⁻⁵ M; in (1:1) aqueous-dioxane; θ = 0.80.
Potentiometric pK₄ = 4.02; pK₅ = 4.70 and 'ε', -0.390°.


<table>
<thead>
<tr>
<th>pH</th>
<th>α(observ) (degree)</th>
<th>α(calculated) (degree)</th>
<th>pH</th>
<th>α(observ) (degree)</th>
<th>α(calculated) (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.06</td>
<td>-0.216</td>
<td>-0.216</td>
<td>5.06</td>
<td>-0.386</td>
<td>-0.386</td>
</tr>
<tr>
<td>2.90</td>
<td>-0.220</td>
<td>-0.221</td>
<td>5.58</td>
<td>-0.390</td>
<td>-0.390</td>
</tr>
<tr>
<td>3.61</td>
<td>-0.225</td>
<td>-0.226</td>
<td>5.88</td>
<td>-0.390</td>
<td>-0.390</td>
</tr>
<tr>
<td>3.85</td>
<td>-0.260</td>
<td>-0.260</td>
<td>6.46</td>
<td>-0.390</td>
<td>-0.390</td>
</tr>
<tr>
<td>4.13</td>
<td>-0.285</td>
<td>-0.286</td>
<td>7.25</td>
<td>-0.390</td>
<td>-0.390</td>
</tr>
<tr>
<td>4.59</td>
<td>-0.310</td>
<td>-0.314</td>
<td>9.25</td>
<td>-0.390</td>
<td>-0.390</td>
</tr>
<tr>
<td>4.80</td>
<td>-0.350</td>
<td>-0.351</td>
<td>9.75</td>
<td>-0.390</td>
<td>-0.390</td>
</tr>
<tr>
<td>4.88</td>
<td>-0.350</td>
<td>-0.353</td>
<td>10.50</td>
<td>-0.390</td>
<td>-0.390</td>
</tr>
</tbody>
</table>

Standard deviation (σ) = ± 0.002

Table-51. Results of rotatometric titration of DBSC (RH₄)
DBSC = 19.23x10⁻⁵ M

<table>
<thead>
<tr>
<th>Species</th>
<th>RH₄⁻</th>
<th>RH₂⁻</th>
<th>RH₃⁻</th>
<th>pH₄</th>
<th>pH₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical rotation in 0.25 dm tube</td>
<td>1) from eqn.(103)</td>
<td>-0.214</td>
<td>-0.314</td>
<td>-0.3147</td>
<td>4.02 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>2) refined</td>
<td>-0.214</td>
<td>-0.3155</td>
<td>-0.3150</td>
<td>4.02 ± 0.04</td>
</tr>
<tr>
<td>Molar Rotation</td>
<td>4,70±0.02</td>
<td>-445.1</td>
<td>-655.2</td>
<td>-311.2</td>
<td>4.02 ± 0.02</td>
</tr>
</tbody>
</table>
Table-52. Rotatometric titrations of DBSC (RH) in presence of Cu, Zn and Cd ions.

<table>
<thead>
<tr>
<th></th>
<th>DBSC + Cu(II)</th>
<th>DBSC + Zn(II)</th>
<th>DBSC + Cd(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>α°(obs.)</td>
<td>α°(calc.)</td>
<td>pH</td>
</tr>
<tr>
<td>2.10</td>
<td>-0.215</td>
<td>-0.215</td>
<td>2.95</td>
</tr>
<tr>
<td>2.64</td>
<td>-0.215</td>
<td>-0.212</td>
<td>3.06</td>
</tr>
<tr>
<td>3.04</td>
<td>-0.200</td>
<td>-0.201</td>
<td>3.28</td>
</tr>
<tr>
<td>5.21</td>
<td>-0.185</td>
<td>-0.185</td>
<td>3.80</td>
</tr>
<tr>
<td>5.38</td>
<td>-0.160</td>
<td>-0.162</td>
<td>3.90</td>
</tr>
<tr>
<td>3.64</td>
<td>-0.130</td>
<td>-0.126</td>
<td>4.13</td>
</tr>
<tr>
<td>3.73</td>
<td>-0.085</td>
<td>-0.094</td>
<td>4.32</td>
</tr>
<tr>
<td>3.96</td>
<td>-0.080</td>
<td>-0.064</td>
<td>4.48</td>
</tr>
<tr>
<td>3.95</td>
<td>+0.050</td>
<td>.....</td>
<td>4.76</td>
</tr>
<tr>
<td>4.11</td>
<td>+0.115</td>
<td>.....</td>
<td>4.94</td>
</tr>
<tr>
<td>4.33</td>
<td>+0.205</td>
<td>.....</td>
<td>5.20</td>
</tr>
<tr>
<td></td>
<td>.....</td>
<td>.....</td>
<td>5.46</td>
</tr>
<tr>
<td></td>
<td>.....</td>
<td>.....</td>
<td>6.04</td>
</tr>
</tbody>
</table>

Standard deviation (σ) = ± 0.0024

Table-55. Results of rotatometric titration of DBSC in presence of Cu²⁺ ions.

<table>
<thead>
<tr>
<th>Species</th>
<th>Cu(DBSC₂⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical rotation 'd' in 0.25 dm tube</td>
<td>+0.116° (refined)</td>
</tr>
<tr>
<td>Molar rotation [M°]₂₀₀ degree mole⁻¹</td>
<td>+201.3°</td>
</tr>
<tr>
<td>Rotatometric log K (refined)</td>
<td>5.29 ± .04</td>
</tr>
<tr>
<td>Potentiometric log K (refined)</td>
<td>5.30 ± .02</td>
</tr>
</tbody>
</table>
The changes in optical rotation of the ligand NBSC (RH₂) during the course of its neutralisation with alkali and complex formation with Zn²⁺ ions have been utilised in the determination of its practical acid dissociation constants (k₂ and k₃), the stepwise formation constants (K₁ and K₂) of its Zn(II) complex Zn(RH)₂⁺ ion and the acid dissociation constants (k₄ and k₅) of the complex ion Zn(RH)₂²⁻. The results are in close agreement with those obtained potentiometrically under identical conditions (Table-38). The molar rotation values of the species RH, RH⁺, RH²⁺, Zn(RH)₂⁺, Zn(RH)₂²⁻ and Zn(RH)₂⁴⁻ have also been found out. Results are stated in Table-37.

Procedure:

A standard 23.95x10⁻² M solution of NBSC was prepared by dissolving 15.825 g of recrystallised NBSC in purified dioxane and making the volume upto 250 ml.

Aliquots of 8.0 ml of this solution together with 4.50 ml of purified dioxane were placed in a number of 25 ml measuring flasks. For the determination of dissociation constants of NBSC, increasing amounts of NaOH solution, requisite amounts of NaClO₄ solution and water were added to each flask to get solutions of different pH values at a constant ionic strength (κ = 0.50) in (1:1) aqueous-dioxane when volumes were made upto the mark with (1:1) aqueous-dioxane as there were contraction in volumes. The solutions were 76.85x10⁻³ M with respect to NBSC in (1:1) aqueous-dioxane. For the determination of formation constants of Zn(RH)₂²⁻ ion and its acid dissociation constants, in addition to 8.0 ml of 23.95x10⁻² M NBSC in dioxane and 4.50 ml of dioxane, 3.15 ml portions of 30.41x10⁻³ M Zn(ClO₄)₂ solution were placed in each flask, increasing amount of NaOH solution, requisite
amount of NaClO₄ solution and water were added and volumes were made upto the mark as stated earlier. Thus each solution contained Zn²⁺:NBSC in the ratio 1:2 in (1:1) aqueous-dioxane at a constant ionic strength (μ = 0.50).

The solutions were allowed to equilibrate. pH values of the solutions and their optical rotations for sodium light were recorded as in the case of DBSC. Data are stated in Tables 34, 35 and 36. Observed rotations were plotted against pH (Fig.36).

Acid dissociation constants (k₁⁺ and k₂⁻) of NBSC:

Optical rotation of NBSC has showed an increase with increase of pH of the solution at pH ≈ 6.50, after which, rotation remained practically constant upto pH ≈ 8.50. At higher pH values rotation has decreased and become negative, till at pH ≈ 12.40, after which rotation has again remained constant, without showing any measurable change on further increasing pH, indicating the end point of the rotatometric titration.

The first rise and final fall in rotation may be attributed to be due to the appearance of new species HH⁺ and RH⁻ respectively as a result of first and second steps of acid dissociation of BH⁺ according to the reactions (40) and (41), for which the step dissociation constants are given by equations (42) and (43) respectively. The region of constant rotation in the pH range 6.5 - 8.5 (Curve I, Fig.36) indicates that the active species present in the solution under this condition is mainly RH⁻ ion. That is, the second step of acid dissociation (41) begins beyond an appreciable gap of pH after the completion of the first step acid dissociation (40).

As k₂⁻ ≫ k₁⁺, the values of pk₂⁻ and pk₁⁺ have been obtained from the plot of α(observable) against pH (Curve I, Fig.36) and also from the plot of \( \frac{d\alpha}{dpH} \) against
Fig. 36
The following the procedure of Irving, Rossotti and Harris, who have employed optical density as the index property - this procedure has been extended taking optical rotation as the index property. The results are stated in Table 38.

The $pK_a$ and $pK_b$ values have also been evaluated considering the first and second steps of ionisation of NSBO separately as follows.

Let $R_3$, $R_2$, $R_1$ be the equilibrium concentrations and $\alpha$, $\beta$, $\gamma$ the molar rotations of the species $RH_3^+$, $RH_2^+$ and $RH_1^-$ respectively and $\alpha$ be the observed rotation in a 0.25 dm tube at any stage of the titration.

Concentration of $RH_2^+$ ion is negligible at the early stages of the titration and consequently the following relations hold good after attainment of equilibrium,

$$ R = R_3 + R_2 $$

$$ \alpha = \frac{R_3}{40} \alpha + \frac{R_2}{40} \beta $$

or $$ \alpha = \frac{aR_3 + bR_2}{R_3 + R_2} $$

and at the later stages after attainment of equilibrium, the relations

$$ R = R_2 + R_1 $$

$$ \alpha = \frac{R_2}{40} \alpha + \frac{R_1}{40} \gamma $$

or $$ \alpha = \frac{bR_2 + cR_1}{R_2 + R_1} $$

exist, when the concentration of $RH_3^+$ is negligibly small. The constants 'a', 'b' and 'c' are the observed optical rotations under the conditions of the experiment.
if the total amount (R) of the ligand NBSC be present as RH₃, RH₂⁻ and RH⁻ respectively. One may get from equations (42) and (117),

$$\text{pH} = \log \left( \frac{a}{b - c} \right) + p_{K_2}$$ ........................ (120)

and from equations (45) and (119) -

$$\text{pH} = \log \left( \frac{a}{b - c} \right) + p_{K_1}$$ ........................ (121)

The values of 'a', 'b' and 'c' have been obtained by measuring optical rotations of solutions containing RH₃ at low pH values and pH values when RH₂NaOH in the ratios 1:1 and 1:2 respectively and also from graphical extrapolation (Curve I, Fig.56). The values have been refined by successive approximation using the values of pk² and pk₁ obtained by the method of Irving, Rossotti and Harris. The pk² and pk₁ values have then been obtained from graphical solution (Curves I and II, Fig.58) of equations (120) and (121) using refined values of 'a', 'b' and 'c'.

Results are stated in Table-58.

The values of calculated α i.e. α(calc.) for the first step of ionisation may be calculated from the relation

$$α_{(\text{calc.})} = \frac{(a + b)}{(b + 1)}$$ ........................ (122)

deduced from equations (42) and (117) and for the second step of ionisation from the relation

$$α_{(\text{calc.})} = \frac{(b + c)}{(b + 1)}$$ ........................ (123)
deduced from equations (43) and (113). Standard deviations (o') have also been calculated using equation (107) and are stated in Table-34.

Molar rotations \( \alpha^0 \) of the species RH\(_2\), RH\(_3\) and RH\(^2\) have been calculated from equation (100) using the refined values of 'a', 'b' and 'c' respectively. Results are stated in Table-37.

**Formation constants (K\(_A\) and K\(_B\)) of the complex Zn(NH\(_2\))\(^{2-}\) ion**

Optical rotation of NBSG solution containing Zn\(^{2+}\) ions has showed a sharp rise with increase of pH and has reached a maximum at pH\(\approx 5.0\), after which rotation has decreased sharply with increase of pH, with change of sign of rotation at pH\(\approx 7.0\), it has reached a minimum at pH\(\approx 7.2\) (Curve II, Fig.36). These sharp rise and fall in rotation should be due to the appearance of some new active species in the solution with increase of pH values and can only be explained if there is complex formation of the ligand NBSG with Zn\(^{2+}\) ions in addition to its stepwise acid dissociations (40) and (41). Complex formation of NBSG with Zn\(^{2+}\) ions may be represented in a stepwise manner by reactions (75) and (76) for which the step formation constants are given by equations (77) and (78) respectively.

Approximate values of the formation constants K\(_A\) and K\(_B\) have been obtained by the method of Irving, Rossotti and Harris\(^{41}\) on plotting \( \frac{\alpha - \alpha'}{\alpha' R} \) against \( \frac{1}{\alpha R} \), where \( \alpha' \) is the optical rotation due to the complexes only. For evaluation of \( \alpha' \) and K\(_A\) the steps (75) and (76) have been considered separately with the idea that at the early stages of this rotametric titration, the reaction (76) occurs and the formation of Zn\((NH)\(^{2-}\) is negligibly small, while at the later stages the reaction (76) occurs exclusively. The acid dissociations of Zn\((NH)\(^{2-}\) is negligible when the formation of complexes take place. Thus
following reactions hold good at the early stages after attainment of equilibrium

\[ M = M_0 + M_1 \]  \hspace{1cm} \ldots \ldots \ldots (124)  
\[ R = R_3 + R_2 + R_1 + M_1 \]  \hspace{1cm} \ldots \ldots \ldots (125)  
\[ \alpha R = a R_2 + b R_1 + \frac{R M_1}{M} \]  \hspace{1cm} \ldots \ldots \ldots (126)  

where \( M \) is the initial concentration of \( Zn^{2+} \) ions, \( M_0 \) and \( M_1 \) are the equilibrium concentrations of \( Zn^{2+} \) ion and the complex \( Zn(RH) \) respectively. \( \alpha \) is the observed optical rotation if the total amount \( (M) \) of \( Zn^{2+} \) ion be present as \( Zn(RH) \). The other notations have their usual meanings. On solving equations (42), (43), (124), (125) and (126) one obtains

\[ R_1 = \frac{R \left( \frac{R M}{M} - \alpha \right)}{(\frac{R M}{M} - \alpha) \left( \frac{R^2 + R}{k R M_2 M_1} \right) (\frac{R M}{M} - \beta) \left( \frac{R^2 + R}{k R^2 M_1} \right) (\frac{R M}{M} - \alpha)} \]  \hspace{1cm} \ldots \ldots (127)  

for the first step of complex formation.

Similarly considering the reaction (76) to occur at later stages, the following relations exist after attainment of equilibrium,

\[ M = M_1 + M_2 \]  \hspace{1cm} \ldots \ldots \ldots (128)  
\[ R = R_3 + R_2 + R_1 + M_1 + 2 M_2 \]  \hspace{1cm} \ldots \ldots \ldots (129)  
\[ \alpha R = a R_2 + b R_1 + \frac{R M_1}{M} + \frac{R M_1}{M} \]  \hspace{1cm} \ldots \ldots \ldots (130)  

where \( M_2 \) is the equilibrium concentration of the complex \( Zn(RH)_2^{2-} \) ion, \( \alpha \) is the observed optical rotation if the total amount \( (M) \) of \( Zn^{2+} \) ion be present as \( Zn(RH)_2^{2-} \). Other notations have their usual meanings. On solving equations (42),
(43), (128), (129) and (130) one obtains

\[ R_1 = \frac{R_4}{(a + \frac{R_4}{N} - \frac{R_5}{N}) + (b + \frac{R_6}{M} - \frac{R_7}{M}) + (c + \frac{R_8}{N} - \frac{R_9}{N})} \quad \ldots \quad (131) \]

for the second step of complex formation. The values of 'd' and 'e' have been obtained from graphical extrapolation (Curve II, Fig. 56) at the maximum at pH ≈ 5.1 and minimum at pH ≈ 7.2 with due correction (r) for excess ligand where necessary. The values of R_1 have been calculated from equations (127) and (131) using the experimental values of 'a', 'b', 'c', 'd', 'e', k_2 and k_4.

Now optical rotation (\( \alpha' \)) due to the complexes may be expressed as

\[ \alpha' = \frac{\alpha N + eN}{M_1 M_2} \quad \ldots \quad \ldots \quad (132) \]

Combining equations (42), (43), (130) and (132) one obtains

\[ \alpha' = \alpha - \frac{\alpha R_1}{N} \quad \ldots \quad \ldots \quad (133) \]

where \( \alpha' = a \frac{R_{10}}{k_{12}} + b \frac{R_{11}}{k_1} + c \).

Now the approximate values of log K_1 and log K_2 may be evaluated from the plot of \( \alpha' \) against pH_1 and also from the plot of \( \frac{\alpha' \delta}{\delta_{pH_1}} \) against \( \frac{1}{2}(pH_1 + pH_2) \) following Irving, Rossotti and Harris. The log K_1 and log K_2 values obtained this way can not be regarded as precisely correct. As the values are very close, the assumption used for calculation of R_1, that the two formation steps occur independently, is not strictly correct. The values of R_1 and hence of \( \alpha' \), log K_1 and log K_2 have been refined by
successive approximation considering both steps (75) and (76) to occur simulta-
neously, when at any stage of the titration after attainment of equilibrium the
relation
\[ N = N_0 + N_1 + N_2 \]  \hspace{1cm} (154)
holds good in addition to (129) and (130). On solving equations (42),(43),(77),
(78),(129),(130) and (154) one may obtain
\[ R^* + L^{-} \rightarrow (a^* - R^0) \]
where \( B = (\alpha - a) \frac{C^+}{k_{1}^*} + (\alpha - b) \frac{C^+}{k_{2}^*} + (\alpha - c) \)
The values of \( R_1 \) have been obtained on solving equation (135) using approximate
values of \( K_1 \) and \( K_2 \) obtained on considering the two formation steps independently.
Refined values of \( K_1 \) and \( K_2 \) have then been obtained on plotting refined values of
\( \alpha^* \) and \( R_1^* \) (Fig.69) by the method of Irving, Rossotti and Harris41 and as well as
from the graphical solution (Fig.40) of the relation
\[ \frac{R^2}{K_1^2} + \left( \frac{Bn^0 - Br_0}{B} \right) \frac{R}{K_1^*} = \frac{1}{K_2} \left( \frac{Br - M_0}{B} - R_1^* \right) - \frac{1}{K_1^*} \]  \hspace{1cm} (136)
which may be deduced from the relation (135). Data and results are stated in
Tables 35 and 38.
Acid dissociation constants \( (k_2 \text{ and } k_3) \) of the complex \( \text{Zn}^{2+}(\text{RH})_2 \) ion:

Optical rotation of solution of NSBG containing \( \text{Zn}^{2+} \) ions has showed a flat rise with increase of pH after reaching a minimum at pH \( \approx 7.20 \), and a second maximum at pH \( \approx 9.20 \) with change of rotation at pH \( \approx 7.80 \) has been observed. Finally rotation has showed a sharp decrease with increase of pH, changes sign at pH \( \approx 9.00 \) and become negative. Above pH \( \approx 11.75 \) rotation has remained constant without showing any appreciable change on further increase of pH. This flat rise and sharp fall in rotation must be due to the appearance of some new active species in the solution and may be ascribed to be due to the species \( \text{Zn}^{2+}(\text{RH})_2^- \) and \( \text{Zn}(\text{RH})_4^- \), formed as a result of stepwise acid dissociation of the complex ion \( \text{Zn}(\text{RH})_2^{2-} \) as represented by

\[
\text{Zn}^{2+}(\text{RH})_2^{2-} \rightleftharpoons \text{Zn}^{2+}(\text{RH})_2^{5-} + \text{H}^+ \quad \cdots \cdots \quad (137)
\]

\[
\text{Zn}^{2+}(\text{RH})_2^{5-} \rightleftharpoons \text{Zn}^{2+}(\text{RH})_4^{4-} + \text{H}^+ \quad \cdots \cdots \quad (138)
\]

for which the successive acid dissociation constants are given by

\[
k_2 = \frac{C_{\text{Zn}^{2+}(\text{RH})_2^{5-}}}{C_{\text{Zn}^{2+}(\text{RH})_2^{2-}}} \text{H}^+ \quad \cdots \cdots \quad (139)
\]

and

\[
k_1 = \frac{C_{\text{Zn}^{2+}(\text{RH})_4^{4-}}}{C_{\text{Zn}^{2+}(\text{RH})_2^{5-}}} \text{H}^+ \quad \cdots \cdots \quad (140)
\]

The constancy of optical rotation with further increase of pH \( > 11.75 \) indicates the end point of the reaction (138), as no more new species could be detected in the solution.

The observed rotations \( 'f' \) and \( 'g' \) due to \( 'M' \) molar solutions of \( \text{Zn}^{2+}(\text{RH})_2^- \) and \( \text{Zn}^{2+}(\text{RH})_4^- \) ions under experimental conditions have been evaluated by graphical...
extrapolation (Curve II, Fig. 36) at the second maximum and at the end point respectively.

The values of \( pK_2 \) and \( pK_1 \) have been obtained by the method of Irving, Rossotti and Harris\(^{41} \) from the plot (Fig. 36) of \( \alpha \) against \( pH \) and also from the maximum and minimum of the plot (Fig. 37) of \( \frac{\Delta \alpha}{\Delta pH} \) against \( \frac{1}{2}(pH' + pH'') \). Data and results are stated in Tables 36 and 38.

The values of \( pK_2 \) and \( pK_1 \) have also been determined considering the two acid dissociation steps (137) and (138) separately as follows.

At the early stages of acid dissociation of \( \text{Zn}(R)^{2-} \) ion, the concentration of the species \( \text{Zn}(R)^{4-} \) ion may be considered negligibly small and consequently the following relations hold good after attainment of equilibrium:

\[
M = M_2 + M_4 \quad \ldots \ldots \quad (141)
\]

\[
R = R_2 + R_4 + R_1 + 2M_2 + 2M_4 \quad \ldots \ldots \quad (142)
\]

and \( \alpha_R = aR_2 + bR_4 + cR_1 + \frac{R_2}{M_2} + \frac{R_4}{M_4} \quad \ldots \ldots \quad (143) \)

and at the later stages after attainment of equilibrium the following relations exist,

\[
M = M_2 + M_4 \quad \ldots \ldots \quad (144)
\]

\[
R = R_2 + R_4 + R_1 + 2M_2 + 2M_4 \quad \ldots \ldots \quad (145)
\]

and \( \alpha_R = aR_2 + bR_4 + cR_1 + \frac{R_2}{M_2} + \frac{R_4}{M_4} \quad \ldots \ldots \quad (146) \)

where \( M_2 \) and \( M_4 \) are the equilibrium concentrations of the species \( \text{Zn}(R)^{2-} \) and \( \text{Zn}(R)^{4-} \) respectively. \( 'I' \) and \( 'I' \) are the observed rotations of \( 'M' \) molar solutions of \( \text{Zn}(R)^{2-} \) and \( \text{Zn}(R)^{4-} \) ions under the conditions of the experiment.
The other notations have their usual meanings. As in the present case $B/M = 2$, then on solving equations (141), (142), and (143) one may get

$$\alpha = \frac{eM_2 + fM_4}{K_2 + K_4} \quad \ldots \ldots \quad (147)$$

and from (144), (145) and (146)

$$\alpha = \frac{fM_5 + gM_6}{M_5 + M_6} \quad \ldots \ldots \quad (148)$$

Finally solving equations (149) and (147) one obtains

$$pH = \log(\frac{\alpha - e}{f - \frac{g}{a}}) + pk_2 + \frac{3 + m}{m} \quad \ldots \ldots \quad (149)$$

and from (140) and (148)

$$pH = \log(\frac{\alpha - e}{f - \frac{g}{a}}) + pk_1 \quad \ldots \ldots \quad (150)$$

The values of $pk_2$ and $pk_1$ have been obtained from the linear plots (Curves I and II, Fig.41) of the equations (149) and (150) respectively using the values of 'e', 'f' and 'g' evaluated by graphical extrapolation (Curve II, Fig.36). Data and results are stated in Tables 36 and 38.

The calculated $\alpha$ values i.e. $\alpha_{(calc.)}$ for the stepwise formation of $Zn(BH)_2^{2-}$ ion have been obtained from the relation

$$\alpha_{(calc.)} = \frac{\lambda(2K_2^2 + \frac{R_1}{K_2} + \frac{1}{K_2}) + R(2K_1 + \frac{1}{K_2})}{\lambda(2K_2^2 + \frac{R_1}{K_2} + \frac{1}{K_2}) + \lambda(2K_1 + \frac{1}{K_2})} \quad \ldots \ldots \quad (151)$$
where \[ A = \frac{C_{H^+}^2}{k_1k_2} + \frac{C_{H^+}}{k_1} + 1 \]
and \[ A' = a \cdot \frac{C_{H^+}^2}{k_1k_2} + b \cdot \frac{C_{H^+}}{k_1} + c \]

which has been obtained from equation (155) and finally \( \alpha' \) from the relation
\[ \alpha'(calc.) = \frac{A'B_1}{B} \]

For successive acid dissociation of \( \text{Zn(HS)}_2^- \) ion, \( \alpha'(calc.) \) values have been obtained from the relations
\[ \alpha'(calc.) = \frac{C_{H^+}^2}{k_2} + f \]
\[ \text{and} \quad \alpha'(calc.) = \frac{C_{H^+}^2}{k_1} + g \]

Standard deviations \( (\sigma') \) have been calculated using the relation (107) and results are stated in Tables 35 and 36.
Table-54. Rototometric titration of NBSC (HCl) at 30 ± 0.5
NBSC, 7.66x10⁻⁴ M; in (1:1) aqueous-dioxane; \( \mu = 0.50 \).
\( a, -0.010^{0} \); \( b, +0.118^{0} \); \( c, -0.410^{0} \).

<table>
<thead>
<tr>
<th>pH</th>
<th>( \alpha_{(\text{obs.})} ) degree</th>
<th>( \alpha_{(\text{calc.})} ) degree (from eqn. 122)</th>
<th>pH</th>
<th>( \alpha_{(\text{obs.})} ) degree</th>
<th>( \alpha_{(\text{calc.})} ) degree (from eqn. 123)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.02</td>
<td>+0.010</td>
<td>+0.012</td>
<td>9.02</td>
<td>+0.100</td>
<td>+0.110</td>
</tr>
<tr>
<td>5.46</td>
<td>+0.010</td>
<td>+0.017</td>
<td>10.01</td>
<td>+0.050</td>
<td>+0.069</td>
</tr>
<tr>
<td>5.99</td>
<td>+0.030</td>
<td>+0.030</td>
<td>10.48</td>
<td>-0.025</td>
<td>-0.001</td>
</tr>
<tr>
<td>4.22</td>
<td>+0.040</td>
<td>+0.040</td>
<td>10.88</td>
<td>-0.100</td>
<td>-0.097</td>
</tr>
<tr>
<td>4.60</td>
<td>+0.055</td>
<td>+0.056</td>
<td>10.95</td>
<td>-0.125</td>
<td>-0.124</td>
</tr>
<tr>
<td>4.76</td>
<td>+0.070</td>
<td>+0.071</td>
<td>11.03</td>
<td>-0.150</td>
<td>-0.147</td>
</tr>
<tr>
<td>4.94</td>
<td>+0.089</td>
<td>+0.082</td>
<td>11.20</td>
<td>-0.200</td>
<td>-0.198</td>
</tr>
<tr>
<td>5.04</td>
<td>+0.086</td>
<td>+0.087</td>
<td>11.36</td>
<td>-0.245</td>
<td>-0.243</td>
</tr>
<tr>
<td>5.28</td>
<td>+0.095</td>
<td>+0.098</td>
<td>11.46</td>
<td>-0.270</td>
<td>-0.268</td>
</tr>
<tr>
<td>5.50</td>
<td>+0.100</td>
<td>+0.103</td>
<td>11.60</td>
<td>-0.300</td>
<td>-0.298</td>
</tr>
<tr>
<td>5.75</td>
<td>+0.105</td>
<td>+0.108</td>
<td>11.77</td>
<td>-0.350</td>
<td>-0.329</td>
</tr>
<tr>
<td>6.41</td>
<td>+0.115</td>
<td>+0.115</td>
<td>11.95</td>
<td>-0.560</td>
<td>-0.558</td>
</tr>
<tr>
<td>7.02</td>
<td>+0.115</td>
<td>+0.115</td>
<td>12.34</td>
<td>-0.580</td>
<td>-0.560</td>
</tr>
<tr>
<td>7.81</td>
<td>+0.115</td>
<td>+0.115</td>
<td>12.45</td>
<td>-0.410</td>
<td>-0.391</td>
</tr>
<tr>
<td>8.42</td>
<td>+0.115</td>
<td>+0.115</td>
<td>13.01</td>
<td>-0.410</td>
<td>-0.408</td>
</tr>
</tbody>
</table>

Standard deviation (\( \sigma \)) = ±0.002 ±0.008
Table-25. Rotatometric titration of NBSC in presence of Zn ions (30 ± 0.5).

MBSC, 76.65 x 10^{-5} M; Zn^{2+}, 38.52 x 10^{-5} M; H=0.50 in (1:1) aqueous-dioxane.

a, +0.010°; b, +0.115°; c, -0.410°; d, +0.245°; e, -0.080°.

Rotatometric $pK_a = 4.61$ and $pK_b = 11.03$.

<table>
<thead>
<tr>
<th>pH</th>
<th>$\alpha$ (obs.)</th>
<th>Taking two steps independently</th>
<th>Taking two steps together (refined values)</th>
<th>$\log K_1$</th>
<th>$\log K_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>degree</td>
<td>$\alpha'$ degree</td>
<td>$\alpha''$ degree</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.60</td>
<td>+0.035</td>
<td>9.60 +0.016</td>
<td>9.24 +0.000</td>
<td>+0.031</td>
<td>-0.004</td>
</tr>
<tr>
<td>5.96</td>
<td>+0.070</td>
<td>9.46 +0.043</td>
<td>9.13 +0.044</td>
<td>+0.072</td>
<td>+0.046</td>
</tr>
<tr>
<td>4.08</td>
<td>+0.090</td>
<td>8.76 +0.060</td>
<td>8.54 +0.061</td>
<td>+0.093</td>
<td>+0.065</td>
</tr>
<tr>
<td>4.21</td>
<td>+0.115</td>
<td>8.55 +0.081</td>
<td>8.33 +0.083</td>
<td>+0.113</td>
<td>+0.094</td>
</tr>
<tr>
<td>4.52</td>
<td>+0.140</td>
<td>8.40 +0.105</td>
<td>8.24 +0.108</td>
<td>+0.142</td>
<td>+0.109</td>
</tr>
<tr>
<td>4.44</td>
<td>+0.175</td>
<td>8.11 +0.128</td>
<td>7.95 +0.146</td>
<td>+0.179</td>
<td>+0.161</td>
</tr>
<tr>
<td>4.65</td>
<td>+0.200</td>
<td>8.00 +0.146</td>
<td>7.85 +0.176</td>
<td>+0.204</td>
<td>+0.186</td>
</tr>
<tr>
<td>4.64</td>
<td>+0.220</td>
<td>7.90 +0.170</td>
<td>7.75 +0.198</td>
<td>+0.222</td>
<td>+0.198</td>
</tr>
<tr>
<td>4.85</td>
<td>+0.250</td>
<td>7.76 +0.207</td>
<td>7.62 +0.230</td>
<td>+0.254</td>
<td>+0.234</td>
</tr>
<tr>
<td>5.05</td>
<td>+0.280</td>
<td>7.56 +0.230</td>
<td>7.42 +0.261</td>
<td>+0.280</td>
<td>+0.247</td>
</tr>
<tr>
<td>5.20</td>
<td>+0.280</td>
<td>7.56 +0.211</td>
<td>7.42 +0.244</td>
<td>+0.284</td>
<td>+0.248</td>
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<tr>
<td>5.28</td>
<td>+0.240</td>
<td>7.35 +0.200</td>
<td>7.22 +0.223</td>
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<tr>
<td>5.40</td>
<td>+0.225</td>
<td>7.22 +0.196</td>
<td>7.09 +0.209</td>
<td>+0.222</td>
<td>+0.205</td>
</tr>
<tr>
<td>5.55</td>
<td>+0.210</td>
<td>7.08 +0.172</td>
<td>7.01 +0.196</td>
<td>+0.210</td>
<td>+0.191</td>
</tr>
<tr>
<td>5.78</td>
<td>+0.190</td>
<td>6.95 +0.149</td>
<td>7.05 +0.168</td>
<td>+0.175</td>
<td>+0.162</td>
</tr>
<tr>
<td>5.85</td>
<td>+0.190</td>
<td>6.90 +0.101</td>
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<td>+0.128</td>
<td>+0.109</td>
</tr>
<tr>
<td>6.02</td>
<td>+0.100</td>
<td>6.87 +0.079</td>
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<td>+0.100</td>
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</tr>
<tr>
<td>6.16</td>
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<td>6.79 +0.079</td>
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<td>+0.085</td>
<td>+0.067</td>
</tr>
<tr>
<td>6.47</td>
<td>+0.050</td>
<td>6.64 +0.037</td>
<td>6.82 +0.037</td>
<td>+0.046</td>
<td>+0.033</td>
</tr>
</tbody>
</table>

Standard deviations ($\sigma$) = 0.003, 0.005.
<table>
<thead>
<tr>
<th>pH</th>
<th>$\alpha^{(obs.)}$ (degree)</th>
<th>$\alpha^{(calc.)}$ (degree) using eqn. (153)</th>
<th>pH</th>
<th>$\alpha^{(obs.)}$ (degree)</th>
<th>$\alpha^{(calc.)}$ (degree) using eqn. (154)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.26</td>
<td>-0.010</td>
<td>-0.012</td>
<td>9.24</td>
<td>+0.045</td>
<td>+0.054</td>
</tr>
<tr>
<td>7.50</td>
<td>-0.005</td>
<td>-0.005</td>
<td>9.55</td>
<td>+0.015</td>
<td>+0.015</td>
</tr>
<tr>
<td>7.76</td>
<td>0.000</td>
<td>0.000</td>
<td>10.09</td>
<td>-0.045</td>
<td>-0.046</td>
</tr>
<tr>
<td>8.02</td>
<td>+0.010</td>
<td>+0.010</td>
<td>10.51</td>
<td>-0.090</td>
<td>-0.079</td>
</tr>
<tr>
<td>8.38</td>
<td>+0.025</td>
<td>+0.025</td>
<td>10.59</td>
<td>-0.125</td>
<td>-0.120</td>
</tr>
<tr>
<td>8.64</td>
<td>+0.035</td>
<td>+0.035</td>
<td>10.88</td>
<td>-0.165</td>
<td>-0.155</td>
</tr>
<tr>
<td>9.02</td>
<td>+0.045</td>
<td>+0.045</td>
<td>11.12</td>
<td>-0.175</td>
<td>-0.175</td>
</tr>
<tr>
<td></td>
<td>....</td>
<td></td>
<td>11.72</td>
<td>-0.200</td>
<td>-0.200</td>
</tr>
<tr>
<td></td>
<td>....</td>
<td></td>
<td>12.10</td>
<td>-0.205</td>
<td>-0.206</td>
</tr>
<tr>
<td></td>
<td>....</td>
<td></td>
<td>12.87</td>
<td>-0.210</td>
<td>-0.210</td>
</tr>
</tbody>
</table>

Standard deviation ($\sigma$) = ±0.004
Fig. 38.
Fig 39
Fig. 40

\[ 2X_{R_1}^{2} + (2(M\bar{x} - R\bar{y}) R_{B}) X 10^9 \]

\[ \left( \frac{R_d - M\bar{x}}{B} \right) R_{B} X 10^9 \]

Fig. 40
Fig. 41
### Table 57. Results of rotatometric titrations of NBSC (RH₃)

<table>
<thead>
<tr>
<th>Species</th>
<th>RH₃</th>
<th>RH₂⁻</th>
<th>RH³⁻</th>
<th>Zn(H)</th>
<th>Zn(H)²⁻</th>
<th>Zn(H)(SH)³⁻</th>
<th>Zn(H)⁴⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical rotation in 0.25 dm tube (degree)</td>
<td>a=+0.010</td>
<td>b=+0.115</td>
<td>c=+0.410</td>
<td>d=+0.848</td>
<td>e=+0.020</td>
<td>f=+0.055</td>
<td>g=0.210</td>
</tr>
<tr>
<td>Molar rotation $\gamma / 0.5$ deg.mole⁻¹</td>
<td>+5.2</td>
<td>+80.0</td>
<td>-214.0</td>
<td>+255.6</td>
<td>-20.9</td>
<td>+67.4</td>
<td>-219.5</td>
</tr>
</tbody>
</table>

### Table 58. Results of rotatometric titrations of NBSC.

pk₂, pk₃, log K₂, log K₃, pk₁ and pk₄ values at 30 ± 0.5°.

<table>
<thead>
<tr>
<th>Plot of $\alpha$ against pH or $\alpha'$ against $pK₁$</th>
<th>Differential plotting</th>
<th>Linear plotting</th>
<th>Average</th>
<th>Potentiometric values at 30 ± 0.5°</th>
</tr>
</thead>
<tbody>
<tr>
<td>pk₂</td>
<td>4.61</td>
<td>4.60</td>
<td>4.61</td>
<td>4.61</td>
</tr>
<tr>
<td>pk₃</td>
<td>11.04</td>
<td>11.02</td>
<td>11.03</td>
<td>11.03</td>
</tr>
<tr>
<td>log K₁</td>
<td>8.59</td>
<td>8.42</td>
<td>8.35</td>
<td>8.39</td>
</tr>
<tr>
<td>log K₂</td>
<td>7.13</td>
<td>7.20</td>
<td>7.22</td>
<td>7.18</td>
</tr>
<tr>
<td>log K₃</td>
<td>15.65</td>
<td>15.62</td>
<td>15.55</td>
<td>15.60</td>
</tr>
<tr>
<td>pk₁</td>
<td>8.21</td>
<td>8.20</td>
<td>8.20</td>
<td>8.20</td>
</tr>
<tr>
<td>pk₄</td>
<td>10.30</td>
<td>10.31</td>
<td>10.30</td>
<td>10.30</td>
</tr>
</tbody>
</table>
It is well known that optical rotation of optically active ligands change during the course of their neutralisation and complex formation with metal ions\(^2,28,45,68,8^\). The changes in optical rotations have been ascribed to be due to the appearance of some new species in the solution. When the active ligand is a weak acid or a weak base, complex formation is accompanied by changes in pH, as a result of that, optical rotation values suffer change with pH. If the reaction occurs in stages and the species formed possess markedly different optical rotations, distinct breaks or inflections may be obtained when the reaction is followed rotatometrically. The rotation maxima or minima in the rotatometric titration curves indicates the rotation due to the newly formed species. The position of such maxima or minima indicates the pH of maximum formation of that species and also the pH range in which it exists. Constancy of rotation with variation of pH indicates the same active species is present in this pH range. Thus the end points of rotatometric titrations can easily be detected.

Distinct steps have been characterised in the rotatometric titrations of NBSG (Curve I, Fig.36). The constancy of rotation in the pH range 6.8-8.5 indicates the only active species present in the solution is \(\text{Rh}_2^2\). The constant rotation at pH values greater than 12.4 is indicative of the end point of the titration. At this stage the solution contains \(\text{Rh}_2^2\) only, the further ionisation of which could not be detected. The successive rise and fall of rotation
(Curve II, Fig. 56) in the rotatometric titration of NBSC in presence of Zn(II) represent the stepwise formation of the species Zn(RH), Zn(RH)²⁻, Zn(RH)³⁻ and Zn(R²)⁴⁻. The exact rotation value due to a particular species is difficult to obtain when there is overlapping of steps. In case of Zn(RH), Zn(RH)²⁻ and Zn(R²)(RH)³⁻ such rotation values have been evaluated by graphical extrapolation with due correction (r) for excess ligand where necessary, that of Zn(R²)⁴⁻ can however be determined experimentally. The first and second steps formation of Zn(RH)²⁻ have been treated separately for the sake of simplicity.

The values of pK₁ and pK₂ obtained rotatometrically are in close agreement with those found potentiometrically. But in the case of log K₁ and log K₂, there are appreciable deviations from potentiometric values. As log K₁ and log K₂ values found are very close, the values obtained by the method of linear plot should be regarded best among the computed ones by different methods. Moreover, these values are in closer agreement with the potentiometric values.

Distinct steps could not be characterised in the rotatometric titration of DBSC (Fig. 32) due to mutual overlapping of its first and second step of ionisations. The end point can however be detected. The rotations due to the species RH²⁻ has been evaluated by graphical extrapolation. Those for the species RH⁴⁻ and RH⁵⁻ have been obtained on successive approximation using the potentiometric values of k₂ and k₄.

Rotatometric titrations of DBSC in presence of Zn(II) and Cd(II) suggests no complex formation at the early stages of titration as the rotation values of the ligand are not changed in presence of these ions, it may be said that the environment of the asymmetric centres do not change. However rotations of DBSC have increased in presence of these ions at comparatively higher pH values. This may be due to formation of DBSC with Zn(II) and Cd(II). But the titrations can
not be completed as precipitation of oxides set in rather very quickly. Formation constants can be calculated, but the results will not be reliable.

Optical rotation of DBSC increases enormously in presence of Cu$^{2+}$ ions. This is definitely due to complex formation of DBSC with Cu(II) forming Cu(RHg)$^-$ in solution and also to the appearance of still newer species Cu(RH)$^-$ and Cu(R)$^{2-}$ as a result of stepwise acid dissociation of Cu(RHg), occurring almost simultaneously with its formation. As a result the rotation due to the species Cu(RHg)$^-$ cannot be obtained by graphical extrapolation. This has been calculated by successive approximation employing the potentiometric value of the formation constant (K). The rotatometric values of pk$^+_d$, pk$^+_l$ of the ligand DBSC and log K for Cu(RHg)$^-$ are in close agreement with those obtained potentiometrically under identical conditions.

All experiments have been performed in the mixed solvent (1:1) aqueous-dioxane. The pH-meter has however been calibrated using standard aqueous buffer solutions. Consequently the values of the acid dissociation constants and formation constants obtained are the so-called "practical" dissociation or formation constants and have no physical significance.

The molar rotation values of the various species involved have been calculated from the experimentally determined or graphically obtained value of observed rotations due to these species under the conditions of the experiment. These are not the absolute values of molar rotations of these species, because optical rotation due to a particular species depends on the environmental factors and wavelength of the light used.