PHYSICO-CHEMICAL STUDIES ON THE FORMATION OF SOME TUNGSTO-TARTRATES AND MOLYBDO-TARTRATES

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ABSTRACT

The viscosity, depression in freezing point, potentiometric and conductometric experiments on the reaction of tartaric acid with sodium tungstate and sodium molybdate indicated the formation of the complex at 1:1 ratio of tungstate or molybdate to tartaric acid. The complex compounds have been isolated. The silver, mercurous, copper, cadmium, zinc, mercuric, barium, strontium, lead, cobalt and nickel salts of tungsto-tartrate and molybdo-tartrate have been prepared from the sodium salt and their composition studied.

INTRODUCTION

Various physico-chemical methods have been adopted to ascertain the formation and nature of tungsto-tartrates and molybdo-tartrates. Rosenheim and Itzig\(^1\) first reported the formation of tungsto-tartrate (\(\text{WO}_3\cdot\text{C}_4\text{H}_6\text{O}_6\))\(^2\) by the reaction of tartaric acid with sodium tungstate. Theodorresco\(^2\)\(^3\) examined tungst-tartrate and molybdo-tartrate complexes by Raman effect. Polarimetric studies on the formation of complex tungsto-tartrates and molybdo-tartrates have been carried out by Britton and Jackson,\(^4\) Murgier and Cordier\(^5\)\(^6\) and Biswas\(^7\)\(^8\). By ultra-microscopic examination, Biswas\(^9\) showed the formation of molybdo-tartrate complex. Dumanskii and D'yachkovskii\(^10\)\(^11\) exposed to light a solution of sodium tungsto-tartrate and attributed the blue colour to the formation of a reduced colloidal complex. Biswas\(^12\) studied the influence of reduction on the optical rotation and showed that the complex does not break into its components by reduction. The formation of tungstate and molybdate complexes with tartaric acid has also been studied by Raman and Vaishya,\(^13\) Delsal,\(^14\) Berkem,\(^15\) Kuan Pan,\(^16\) Banerjee and Bhattacharya\(^17\) and Baillie and Brown.\(^18\) Pogainis and Shaw\(^19\) prepared tetra sodium tungsto-tartrate,
Physico-Chemical Studies on Tungsto-Tartrates and Molybdo-Tartrates

Na₄C₄H₆O₆·WO₃·8H₂O, by the reaction of sodium tungstate and sodium tartrate. Sarju Prasad and Krishnaiah studied the sodium tungstate-tartaric acid system by viscosity and depression in freezing point measurements and indicated the formation of a complex at 1:1 ratio of the components. The complex has been isolated by two different methods.

In the present investigation, the tungstate and molybdate complexes with tartaric acid have been studied by various physico-chemical methods. Further, attempts have been made to establish the existence of complex anions, tungsto-tartrate \((WO₃·C₄H₄O₆)\)⁻⁻ and molybdo-tartrate \((MoO₃·C₄H₄O₆)\)⁻⁻ as such in solution.

**Experimental**

All the chemicals used were of B.D.H. or Merck’s ‘extra pure’ quality. Solutions of sodium molybdate (M/2) and tartaric acid (IM) were prepared. The mono-variation system was followed in determining the viscosity and depression in freezing point of the mixed solutions. The volume of sodium molybdate (20 c.c.) was fixed and that of tartaric acid was varied and the total volume was made up to 50 c.c. with distilled water.

*Viscosity.*—The time of flow of the above solutions and water was determined by Ostwald’s viscometer at 30 ± 0.05°C by placing the viscometer in a thermostat of Townson & Mercer company. The viscosity of the solutions was calculated using the equation,

\[
\frac{n_1}{n_w} = \frac{d_1t_1}{d_w t_w}
\]

where \(n_1\), \(d_1\) and \(t_1\) represent the viscosity, density and time of flow respectively for the solution and \(n_w\), \(d_w\) and \(t_w\) those for water. A graph was plotted representing viscosity against the volume of tartaric acid and the maxima in the Curve (Fig. 1, Curve I) was taken to be due to complex formation.

*Freezing point.*—The freezing point of water and the solutions was determined by Beckmann’s freezing point method and the depression in the freezing point plotted against the volume of tartaric acid.

*Potentiometric titration.*—M/10 solutions of sodium tungstate, sodium molybdate and tartaric acid were prepared. The cell employed takes the form

\[
\text{Pt} \quad \{ \text{Quinhydrone (satd.) in solution of unknown pH} \} \quad \{ \text{Satd. KCl} \} \quad \{ \text{salt bridge} \} \quad \text{Calomel electrode.}
\]
The measurement of potentials was taken by Pye model potentiometer and a sensitive mirror galvanometer was used to determine the null point.

10 c.c. of tartaric acid was taken in the titration vessel and relative voltage (E) of the above cell was determined at the room temperature by balancing it against an accumulator cell. Sodium tungstate or sodium molybdate solution was added from the burette and after each addition the solution was mixed well and the voltage measured. The end-point of the titration is given by the point of inflection on the curve representing the values of \( \Delta E/\Delta V \) against volume of sodium tungstate (Fig. 3, Curve I) or sodium molybdate (Fig. 3, Curve II).

Conductometric titration.—Conductivity water was used for the preparation of standard solutions and for further dilutions. M/100 solutions of sodium tungstate and sodium molybdate and M/10 tartaric acid solution...
were prepared. 10 c.c. of sodium tungstate or molybdate diluted to 60 c.c. was placed on a magnetic stirrer and the dip cell was properly dipped in the solution. The titration cell was immersed in a thermostat to control the temperature of the solution within $\pm 0.1^\circ$ C. The conductance was measured by Mullard conductivity bridge type E7566 with direct reading visual balance detector. Tartaric acid was added from a micro-burette in small amounts, the solution stirred well and the conductance was recorded. The curves were drawn between the conductance and the volume of tartaric acid. The equivalence point was determined by the point of intersection of the two portions of the curves.

An examination of Fig. 2 (Curve I) and Fig. 3 (Curve I) lead to exactly analogous conclusions obtained by viscometric and depression in freezing point measurements (loc. cit.) and are in conformity with polarimetric and Raman effect studies (loc. cit.). Also the viscometric (Fig. 1, Curve I), Cryoscopic (Fig. 1, Curve II), potentiometric (Fig. 3, Curve II) and conductometric (Fig. 2, Curve II) studies of sodium molybdate-tartaric acid system yielded unequivocal results leading to identical conclusions, indicating the formation of a complex at 1:1 ratio of the components.
Isolation of complex compounds.—Sodium tungsto-tartrate has been isolated earlier (loc. cit.) by two different methods. Similar methods have been tried to isolate sodium molybdo-tartrate complex. It may be interesting to note that this compound can be crystallized and dried over calcium chloride in a desiccator and no addition of alcohol is necessary to separate the compound. Also the duration of time required to dissolve equimolecular proportions of molybdic and tungstic acids into a solution of alkali tartrate may be shown as,

\[ \text{molybdic} < \text{tungstic}. \]

The potassium and ammonium salts of tungsto-tartrate and molybdo-tartrate can be prepared by using potassium or ammonium tartrate instead of sodium tartrate and dissolving tungstic or molybdic acid in the tartrate solution in equimolecular proportions.

Further, to confirm the existence of complex anions (tungsto-tartrate and molybdo-tartrate) as such in solution, the silver, mercurous, copper,
cadmium, zinc, mercuric, barium, strontium, lead, cobalt and nickel salts of tungsto-tartrate and molybdo-tartrate were prepared by adding excess of a moderately strong solution of the above metallic nitrates to a solution of sodium tungsto-tartrate or molybdo-tartrate. Generally, an immediate precipitation took place, which was filtered, washed with water, filter-pressed and finally dried over calcium chloride in a vacuum desiccator. However, zinc, cobalt and nickel tungsto-tartrates separated only after shaking for a long time. But copper, zinc, cobalt and nickel molybdo-tartrate did not separate even after long shaking. So these systems have been studied conductometrically. 10 c.c. of M/100 solution of copper sulphate (Fig. 4, Curve I), zinc sulphate (Fig. 4, Curve II), cobalt nitrate (Fig. 4, Curve IV) or nickel nitrate (Fig. 4, Curve III) diluted to 60 ml. was conductometrically titrated against M/10 sodium molybdo-tartrate. An examination of the Curves I-IV in Fig. 4 shows the formation of the corresponding salts at 1:1 ratio of the components.

![Fig. 4](image-url)
TABLE I

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Compound</th>
<th>Colour</th>
<th>% Tungsten</th>
<th>% Other metal</th>
<th>% H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found</td>
<td>Calc.</td>
<td>Found</td>
</tr>
<tr>
<td>1</td>
<td>K₂(WO₃•C₄H₄O₆)•C₄H₅OH</td>
<td>White</td>
<td>36.28</td>
<td>36.50</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>(NH₄)₂(WO₃•C₄H₄O₆)•C₄H₅OH</td>
<td></td>
<td>39.60</td>
<td>39.83</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ag₄(WO₃•C₄H₄O₆)</td>
<td></td>
<td>30.25</td>
<td>30.87</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Hg₄(WO₃•C₄H₄O₆)</td>
<td></td>
<td>23.01</td>
<td>23.55</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Pb(WO₃•C₄H₄O₆)</td>
<td></td>
<td>31.26</td>
<td>31.34</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Cu(WO₃•C₄H₄O₆)•4H₂O</td>
<td>Peacock</td>
<td>35.80</td>
<td>35.70</td>
<td>12.37</td>
</tr>
<tr>
<td>7</td>
<td>Zn(WO₃•C₄H₄O₆)•H₂O</td>
<td>White</td>
<td>39.38</td>
<td>39.70</td>
<td>13.00</td>
</tr>
<tr>
<td>8</td>
<td>Cd(WO₃•C₄H₄O₆)•H₂O</td>
<td></td>
<td>35.56</td>
<td>36.03</td>
<td>20.94</td>
</tr>
<tr>
<td>9</td>
<td>Hg₂(WO₃•C₄H₄O₆)</td>
<td></td>
<td>29.94</td>
<td>31.70</td>
<td>35.25</td>
</tr>
<tr>
<td>10</td>
<td>Ba(WO₃•C₄H₄O₆)</td>
<td></td>
<td>38.02</td>
<td>35.56</td>
<td>24.02</td>
</tr>
<tr>
<td>11</td>
<td>Sr(WO₃•C₄H₄O₆)</td>
<td></td>
<td>38.18</td>
<td>39.34</td>
<td>17.99</td>
</tr>
<tr>
<td>12</td>
<td>Co(WO₃•C₄H₄O₆)•2H₂O</td>
<td>Light blue</td>
<td>37.85</td>
<td>38.74</td>
<td>12.18</td>
</tr>
<tr>
<td>13</td>
<td>Ni(WO₃•C₄H₄O₆)•2H₂O</td>
<td>Parrot green</td>
<td>37.43</td>
<td>38.77</td>
<td>11.88</td>
</tr>
</tbody>
</table>

TABLE II

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Compound</th>
<th>% Molybdenum</th>
<th>% Other metal</th>
<th>% H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Found</td>
<td>Calc.</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Na₄(MoO₃•C₄H₄O₆)•H₂O</td>
<td>27.03</td>
<td>26.98</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>K₄(MoO₃•C₄H₄O₆)•H₂O</td>
<td>24.45</td>
<td>24.74</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(NH₄)₂(MoO₃•C₄H₄O₆) •H₂O</td>
<td>27.67</td>
<td>27.74</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Ag₄(MoO₃•C₄H₄O₆)</td>
<td>18.21</td>
<td>18.90</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Hg₄(MoO₃•C₄H₄O₆)</td>
<td>13.98</td>
<td>13.86</td>
<td>50.93</td>
</tr>
<tr>
<td>6</td>
<td>Pb(MoO₃•C₄H₄O₆)</td>
<td>20.30</td>
<td>19.23</td>
<td>40.71</td>
</tr>
<tr>
<td>7</td>
<td>Cd(MoO₃•C₄H₄O₆)•2H₂O</td>
<td>20.78</td>
<td>21.80</td>
<td>26.48</td>
</tr>
<tr>
<td>8</td>
<td>Hg₂(MoO₃•C₄H₄O₆)</td>
<td>20.27</td>
<td>19.19</td>
<td>41.23</td>
</tr>
<tr>
<td>9</td>
<td>Ba(MoO₃•C₄H₄O₆)</td>
<td>22.58</td>
<td>22.37</td>
<td>30.87</td>
</tr>
<tr>
<td>10</td>
<td>Sr(MoO₃•C₄H₄O₆)</td>
<td>24.87</td>
<td>25.29</td>
<td>22.75</td>
</tr>
</tbody>
</table>

* All the compounds are white in colour.
Analysis.—Molybdenum was estimated as PbMoO₄, tungsten as WO₃, copper iodimetrically, silver as chloride, barium, strontium and lead as sulphates, cadmium and zinc as pyrophosphates, mercury as sulphide, cobalt as pyridine thiocyanate complex and nickel as dimethylglyoxime complex. The alcohol and water contents in the compounds were estimated by finding the loss in weight of the compound at 80°C. and 105°C. respectively.

The results of analysis of the various tungsto-tartrates and molybdo-tartrates are presented in Tables I and II.

An examination of the above results confirm the existence of the complex anions (tungsto-tartrate⁻⁻ and molybdo-tartrate⁻⁻) as such in solution. It may be interesting to note that the molybdo-tartrates are comparatively less stable than tungsto-tartrates and are susceptible to reduction to the blue-coloured lower oxides.

ACKNOWLEDGEMENTS

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