Studies on ion-pairing effects of the kinetics of aquation of bromopentaammin cobalt(III) complex in malonate media

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Dicarboxylic acid
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1. Introduction

Transition metal complexes play a variety of important roles in biological systems. The biological activities of cobalt complexes have been the subject of studies on the inhibition of rabbit brain and the inhibition of soybean lipoxigenase enzyme [1-2]. Also cobalt(II) is beneficial for human since it is a part of vitamin B12 [3].

Different studies had described the kinetics of aquation of halogenopentaamminecobalt(III) in different media [4-8]. Such investigations include numerous factors, describing preferential, selective and specific solute-solvent interactions and are useful in accounting for the equilibrium behavior of electrolytes in solution. It was shown [9] that the ion-pairs formed between some bivalent anions and halopentaammine cobalt(III) and chromium(III) cations undergo aquation at a faster rate compared to the free cations. It was found that [10] the ion-pairing effects on the rate of aquation of bromopentaammine cobalt(III) perchlorate in 20% (v/v) ethylene glycol solutions of some dicarboxylates must follow Waytt and Davies [11] treatment for calculating the ion-pair rate coefficients. It is fairly established that halopentaammine cobalt(III) complexes aquated by an essentially dissociative process [12].

The aim of the present work is to study the aquation of bromopentaamminecobalt(III) perchlorate in malonate buffer solutions [0.008-0.040 mol/L malonic acid neutralized by 80% Na2CO3 containing tert-butanol (10%-50%, v/v)] in an attempt to determine the solvent effects on thermodynamic and extrathermodynamic parameters of activation where the data can be linked to obtain information about the solute-solvent interaction.

2. Experimental

2.1. Reagents

Cobalt(II) carbonate, hydrobromic acid 48%, ammonia, malonic acid, sodium carbonate and tert-butanol were purchased from Fluka Chemika. Hydrogen peroxide, were purchased from Riedel-de Haën. Hydrochloric acid was purchased from Chemical Management Consulting. Perchloric acid 60% was purchased from Merck. The bromopentaammine cobalt(III) perchlorate complex was prepared by using the method of Hynes [13].

2.2. Procedure

The rate of aquation of [Co(NH3)6Br](ClO4)2 complex in 10%-50% (v/v) of tert-butanol with malonate buffer solution at 30-60 °C was followed spectrophotometrically using Unicam Helios Alpha and Beta spectrophotometer at λ = 250 nm. The spectrophotometer was fitted with thermostated cell holders, heated by water circulating from a Heto HMT 200 thermostat. The inflow and the outflow temperatures were measured and the mean temperature was taken as that of the cell.
Table 1. Values of rate constants (k_{obs} x 10^6) in sec^{-1} for the aquation of [Co(NH$_3$)$_5$Br]$^{2+}$ in tert-butanol (10-50%) at different temperatures.

<table>
<thead>
<tr>
<th>T, °C</th>
<th>10% tert-butanol</th>
<th>20% tert-butanol</th>
<th>30% tert-butanol</th>
<th>40% tert-butanol</th>
<th>50% tert-butanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>2.96</td>
<td>2.68</td>
<td>0.11</td>
<td>0.61</td>
<td>4.45</td>
</tr>
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<td>3.32</td>
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<td>40</td>
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<td>4.83</td>
<td>18.30</td>
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<tr>
<td>50</td>
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<td>93.90</td>
<td>95.70</td>
<td>44.80</td>
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<td>364.00</td>
<td>224.00</td>
<td>227.00</td>
<td>208.00</td>
<td>180.00</td>
</tr>
</tbody>
</table>

Table 2. Values of rate constants (k_{obs} x 10^6) for the aquation of [Co(NH$_3$)$_5$Br]$^{2+}$ in malonate media (m$_1$) containing tert-butanol (10-50%) at different temperatures.

<table>
<thead>
<tr>
<th>m$_1$, mol/L</th>
<th>Temperature, °C</th>
<th>10% tert-butanol</th>
<th>20% tert-butanol</th>
<th>30% tert-butanol</th>
<th>40% tert-butanol</th>
<th>50% tert-butanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>35</td>
<td>40</td>
<td>50</td>
<td>60</td>
</tr>
<tr>
<td>0.008</td>
<td></td>
<td>4.71</td>
<td>14.64</td>
<td>29.17</td>
<td>58.77</td>
<td>473.1</td>
</tr>
<tr>
<td>0.016</td>
<td></td>
<td>5.08</td>
<td>11.95</td>
<td>34.06</td>
<td>141.2</td>
<td>394.1</td>
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<tr>
<td>0.024</td>
<td></td>
<td>5.71</td>
<td>17.28</td>
<td>47.44</td>
<td>163.95</td>
<td>469.4</td>
</tr>
<tr>
<td>0.032</td>
<td></td>
<td>2.07</td>
<td>26.53</td>
<td>38.78</td>
<td>164.81</td>
<td>546.1</td>
</tr>
<tr>
<td>0.04</td>
<td></td>
<td>3.99</td>
<td>20.1</td>
<td>47.34</td>
<td>187.23</td>
<td>546.1</td>
</tr>
</tbody>
</table>

3. Results and discussion

Plots of log (A-A*) versus time were found to be linear for the aquation of [Co(NH$_3$)$_5$Br]$^{2+}$ complex. The observed rate constants are collected in Table 1 and 2.

The ion-pair rate coefficient $k_0$ was calculated according to the following Wyant and Davis equation [11]:

$$k_{obs} = k_0 [\text{CpX}^2+] + k_{ip} [\text{CpXL}]$$

where, $k_0$ - the observed rate constant in the absence of dicarboxylate ion, $k_{ip}$ - the observed rate constant in the presence of dicarboxylate ion, $m_3$ - the stoichiometric concentration of the complex salt, $[\text{CpX}^2+]$ - the free complex ion concentration and $[\text{CpXL}]$ - the ion-pair concentration. $[\text{CpXL}]$ was calculated with the aid of the following equations:

$$[\text{CpXL}] = [\text{CpX}^2+] + L^2$$  \hspace{0.5cm} (2)

$$[\text{NaL}^+] = 2m_2 - [\text{NaL}^-] - [\text{NaL}^+]$$  \hspace{0.5cm} (3)

$$[\text{H}_2\text{L]} = [\text{HL}^-] + [\text{CpXL}] + [\text{NaL}^-] + [\text{NaL}^+]$$  \hspace{0.5cm} (4)

$$[\text{HL}^-] = [\text{L}^2+] + [\text{H}^+]$$  \hspace{0.5cm} (5)

where:

$$K_0 = [\text{CpX}^2+][L^2]/[\text{CpXL}]$$  \hspace{0.5cm} (6)

$$K_1 = [\text{H}^+][\text{HL}^-]/[\text{H}_2\text{L}]$$  \hspace{0.5cm} (7)

$$K_2 = [\text{H}^+][L^2]/[\text{HL}^-]$$  \hspace{0.5cm} (8)

$$K_{NaL} = [\text{Na}^+][L^2]/[\text{NaL}^-]$$  \hspace{0.5cm} (9)

$$\log \gamma_i = -A(1^{1/2}/(1+1.3I^{1/2})-0.3I)$$ (Debye-Huckle equation)

$$I = 0.5 ([\text{H}^+] + [\text{HL}^-] + 4[L^2+] + 4[\text{CpX}^2+] + 2m_3 + [\text{Na}^+] + [\text{NaL}^-])$$

$$m_1 = [\text{H}_2\text{L}] + [\text{HL}^-] + [\text{CpXL}] + [\text{NaL}^-]$$

$$m_3 = [\text{CpX}^2+] + [\text{CpXL}]$$

The principle of calculations performed by computer programs can be summarized as:

For the first cycle $[\text{H}^+] = 0$, $[\text{CpXL}] = 0$, $[\text{NaL}^-] = 0$, $m_2 = 0.5m_3$, $[\text{H}_2\text{L}] = 0.3m_3$, $[\text{HL}^-] = m_1 - [\text{H}_2\text{L}] - [\text{CpXL}] - [\text{NaL}^-] - [\text{H}_2\text{L}])$, $[\text{Na}^+] = 2m_2 - [\text{NaL}^-]$. Afterward, the ionic strength takes its first approximated value and then $\gamma_1$ and $\gamma_2$ after which the following terms take their new value;
Then I, $\gamma_1$, and $\gamma_2$ were recalculated again. These steps of calculations were repeated many times until the difference between two successive values of [CpXL] becomes equal to or less than $10^{-7}$. The obtained average values of $k_{ip}$ in malonate media with different percentage of tert-butanol are collected in Table 3.

### Table 3. Calculated values of rate constants ($k_{ip} \times 10^9$) in sec$^{-1}$ for the aquration of [Co(NH$_3$)$_5$Br]$^{2+}$ in malonate buffer containing tert-butanol (10-50%) at different temperatures.

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>4.43</td>
<td>4.39</td>
<td>2.39</td>
<td>0.39</td>
<td>0.71</td>
</tr>
<tr>
<td>30</td>
<td>16.46</td>
<td>1.04</td>
<td>4.16</td>
<td>0.86</td>
<td>1.36</td>
</tr>
<tr>
<td>35</td>
<td>28.22</td>
<td>2.59</td>
<td>7.10</td>
<td>1.83</td>
<td>2.56</td>
</tr>
<tr>
<td>40</td>
<td>47.54</td>
<td>6.32</td>
<td>11.92</td>
<td>3.79</td>
<td>4.73</td>
</tr>
<tr>
<td>50</td>
<td>120.60</td>
<td>34.56</td>
<td>32.00</td>
<td>15.26</td>
<td>15.19</td>
</tr>
<tr>
<td>60</td>
<td>327.60</td>
<td>170.60</td>
<td>80.98</td>
<td>56.42</td>
<td>45.54</td>
</tr>
</tbody>
</table>

#### 3.1. Variation of ion-pair coefficients ($k_{ip}$) with solvent parameters

The effect of water concentration in aqueous organic solvent mixture was investigated by the plot of the Log $k_{ip}$ versus Log [H$_2$O] at 30 °C. This plot was found to be nonlinear as shown in Figure 1. This nonlinearity confirms that the internal structure of the media studied suffered from serious changes on addition of tert-butanol in the presence of malonate buffer, indicating that the hydrogen bond between the organic solvent and the buffer added to water is stronger than between two water molecules. Thus, hydrogen bonding between neighboring water molecules will be replaced gradually by hydrogen bonding with solvent and buffer molecules where the tetrahedral structure of water is largely broken [14].

![Figure 1. Log $k_{ip}$ versus log [H$_2$O] at 30 °C at different concentrations of Malonate buffer.](image1.png)

However, Elsemongy and Amira [22] proposed a general equation for the variation of specific rate constant ($k$) with the dielectric constant (D) for any reaction, in which the transition state may or may not polarized. This equation was proved to be applicable to usual reactions, as well as those exhibiting minima or maxima with solvent composition variation. Their equation takes the following for

$$\log A/K = E_b/2.302.R \log C/D$$  \hspace{0.5cm} (25)

$$\log C = \log A + 293.15b$$  \hspace{0.5cm} (26)

Tert-butanol has special effect on the formation of ion-pair. This fact was also proven in previous studies [15-16], where it was found that tert-butanol has a greater effect on the water structure than the other solvents used earlier due to its branched chain. This may be attributed to the variation of important properties of the medium, such as the structure of the solvent, ionizing power, basicity and dielectric constant, which greatly influence the rate of the reaction. In addition, tert-butanol is a dipolar protic solvent [17], since the oxygen atom of an alcohol molecule carries one proton and two lone pairs of electrons; it might have been expected to form three hydrogen bonds with its neighbors, but the evidences show that no more than two bonds are formed, each oxygen acting once as proton donor and once as proton acceptor due to steric effects of the alkyl groups. Also Log $k_{ip}$ was plotted against reciprocal of the dielectric constant D at 25 °C, where the dielectric constant values of different compositions are obtained from Akerlof data [18]. As shown in Figure (3), the plot was found to be non linear in accordance with the general observations found in the auration of a large number of other cobalt(HI) complexes [19-20] in water-cosolvent mixtures, which led to a conclusion, that the contribution of the non electrostatic part of solvent effect, overcomes the electrostatic component part. Also, these parameter measures macroscopic properties, while specific solute-solvent interactions occur on a microscopic scale are completely neglected. In such cases, the differential solvation of the initial and transition states is the controlling factor for the changes in the rate constant [21].

![Figure 2. Log $k_{ip}$ versus Y at 25 °C at different concentrations of Malonate buffer.](image2.png)

![Figure 3. Log $k_{ip}$ versus 1/D at 30 °C at different percentages of tert-butanol in Malonate buffer media.](image3.png)
where A is the frequency factor, a and b are Akerlof’s empirical constants [17]. The plot Log A/K versus Eb/Log G/D as shown in Figure 4, gives a good straight line with a slope approximately equals to 0.052, which is equal to 1/2.302R = 0.052. This result adds a further support of the validity of the above equation in the case of aquation of bromopentaamminecobalt(III) complex ion in water-tert-butanol medium.

3.2. Thermodynamic parameters of the ion-pair reactions

The thermodynamic parameters of the activated complex at 40 °C were collected in Table 4.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>x2 (Mole fraction)</th>
<th>ΔHIp kJ/mole</th>
<th>ΔSiP J/K.mole</th>
<th>ΔSiS kJ/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.02</td>
<td>81.11</td>
<td>-49.81</td>
<td>96.69</td>
</tr>
<tr>
<td></td>
<td>0.045</td>
<td>140.23</td>
<td>122.51</td>
<td>101.94</td>
</tr>
<tr>
<td></td>
<td>0.075</td>
<td>80.50</td>
<td>-63.23</td>
<td>100.29</td>
</tr>
<tr>
<td></td>
<td>0.112</td>
<td>114.42</td>
<td>35.62</td>
<td>103.27</td>
</tr>
<tr>
<td></td>
<td>0.116</td>
<td>95.66</td>
<td>-22.49</td>
<td>102.42</td>
</tr>
</tbody>
</table>

A linear plot of ΔGIp against ΔGass (free energy of ion-pair formed) is obtained as shown in Figure 5, which takes the form,

\[ ΔGIp = a'ΔGass^0 + b' \] (27)

![Figure 5. ΔGIp versus ΔGass for Malonate buffer at different solvent compositions at 40 °C.](image)

The relationship between the enthalpy of activation ΔHIp and the enthalpy of association (ion-pair formation) ΔHass0 at different solvent compositions is shown in Figure 6. The plot shows a linear correlation which takes the form of Equation (28):

\[ ΔHIp = cΔHass0 + d' \] (28)

This behavior is due to the interaction between the mixed solvent medium containing the dicarboxylate anions and water. These interactions are attributed to the essentially co-operative nature of hydrogen bonding; together with the unfavorable steric effect of the organic group for both the tert-butanol and the malonate buffer. Thus, it restricts the degree of order, which can be established in the liquid state, and precludes the kind of three dimensional associations which is dominant in water.

![Figure 6. ΔHIp versus ΔHass0 for Malonate buffer at different solvent compositions at 40 °C.](image)

Finally, the plots of ΔSiP versus ΔSiS0 for different solvent compositions are also found to be linear as represented in Figure 7 according to Equation (29):

\[ ΔSiP = eΔSiS0 + f \] (29)

The obtained correspondence suggests that both entropies of activation ΔSiP and association ΔSiS are largely charge-controlled.

![Figure 7. ΔSiP versus ΔSiS0 for Malonate buffer at different solvent compositions at 40 °C.](image)

3.3. Variation of activation parameters with solvent composition

The variation of the thermodynamic parameters of activation ΔGIp, ΔHIp and ΔSiP with the mole fraction of the tert-butanol x2 is introduced in Figure 8 at different composition of tert-butanol. ΔHIp and ΔSiP plots versus mole fraction of the co-solvent x2 displayed extrema at different values of x2, indicating that the addition of tert-butanol in small amounts plays an important role. This was also observed for trans-[CopyCl+]1+ [23] and [Co (NH3)5Br]+ [24] where the structure formation becomes greater at lower values of x2. At the lower x2 (between 20% to 30% v/v of tert-butanol), the water is rich in the media where the tert-butanol molecules progressively occupy the cavities in the water network without enhancing the water structure. However, with an increase in the tert-butanol concentration, the water structure undergoes a gradual disruption and clusters are formed through the formation of hydrogen bonding. By adding more and more tert-butanol, it...

![Figure 8.](image)
has characteristics that the alkyl groups cooperative ordering of water molecules by a hydrophobic hydration effect.

The changing of solvent composition has little effect on ΔG\text{ip} as shown in Table 4 by which linear plots are observed between ΔG\text{ip} against x\text{ip}, indicating the presence of compensation effect between ΔH\text{ip} and ΔS\text{ip}.

![Figure 8. ΔH\text{ip}, ΔS\text{ip} and ΔG\text{ip} versus x\text{i} for Malonate buffer at different solvent compositions.](image)

Figure 9 shows the plots of ΔH\text{ip} versus ΔS\text{ip} for the ion-pair aquation reactions at different compositions of tert-butanol with an isokinetic temperature, β=58 °C, which lies within the temperature range studied (30-60 °C), this emphasizes the compensation effect. The true explanation of compensation effect lies in solute-solvent interactions, where the interaction between the solute and one of the solvent components, which is tert-butanol, is particularly strong. This will lower the enthalpy; it will also, by restricting the freedom of vibration and of rotation of the solvent molecules, will lower the entropy.

![Figure 9. ΔH\text{ip} versus ΔS\text{ip} for Malonate buffer at different solvent compositions at 60 °C.](image)

3.4. Variation of free energy of transfer with solvent composition

It has long been recognized that the solvolysis reactions of Co(III) complexes [25,26], proceed via the l\text{I} mechanism [27,28] involving the rate-determining loss of the halide ion according to the following equations:

\begin{equation}
\text{[Co(NH}_3\text{)]}^{2+} \rightleftharpoons \text{[Co(NH}_3\text{)]}^3^+ + \text{X} \tag{30}
\end{equation}

\begin{equation}
\text{[Co(NH}_3\text{)]}^{2+} + \text{H}_2\text{O} \rightarrow \text{[Co(NH}_3\text{H}_2\text{O]}^3^-} \tag{31}
\end{equation}

The extreme extension of Co-X bond in the transition state is revealed by a comparison of the volumes of activation with the overall volume changes for related Co(III) complexes. The situation affects the ions in the transition state to be independently solvated, which allows the application of a free energy cycle constructed by Wells [29], relating the process initial state into transition state for the aquation of the six co-ordinated complex [Co(NH\text{3})\text{X}]^2\text{+} to give five co-ordinated [Co(NH\text{3})\text{X}]^2\text{+} intermediate together with the halide ion in the transition state in water (W) and in the mixed solvent (S) [29-30] according to the following scheme:

Initial state transition state

\[ \text{[Co(NH}_3\text{)]}^{2+} + \text{X} \rightarrow \text{[Co(NH}_3\text{)]}^3^+ + \text{X} \tag{32} \]

where ΔG\text{f} is the activation free energy in the medium (i = W for water and S for the mixed solvent). Equation (32) results from this cycle, where ΔG\text{f}(i) is the free energy of transfer of species (i) between water and the mixed solvent.

\[ \Delta G\text{f}(i) = \Delta G\text{f}[\text{Co(NH}_3\text{)}]^{3+} + \Delta G\text{f}[\text{Co(NH}_3\text{X}]^2\text{+} \tag{33} \]

Converting free energies of activation, ΔG\text{f}, into rate constant (32) can be rearranged to Equation (33):

\[ 2.303.R.T.\log \frac{k_w}{k_s} \Delta G\text{f}(i) = \Delta G\text{f}[\text{Co(NH}_3\text{)}]^{3+} + \Delta G\text{f}[\text{Co(NH}_3\text{X}]^2\text{+} \tag{34} \]

which relates the rate constant with non-electrostatic component of the solvent mixture.

While applying the free energy cycle for the ion-pair effect on the aquation of the bromopentaamminecobalt(III) complex ion in the dicarboxylates media follow the following equations:

\[ \text{L}^2\text{...[Co(NH}_3\text{)]}^{2+} \rightarrow \text{[Co(NH}_3\text{)]}^3^+ + \text{X} \tag{34} \]

\[ \text{L}^2\text{...[Co(NH}_3\text{)]}^{2+} + \text{H}_2\text{O} \rightarrow \text{[Co(NH}_3\text{H}_2\text{O]}^3^-} \tag{35} \]

However, Equation (33) can be converted to Equation (36)

\[ 2.303.R.T.\log \frac{k_w}{k_s} \Delta G\text{f}(i) = \Delta G\text{f}[\text{Co(NH}_3\text{)}^{3+} - \text{Co(NH}_3\text{X}]^2\text{+} \tag{36} \]

Values of k\text{0} and k\text{ip} at 25 °C were obtained from the interpolation of Arrhenius plot and values of ΔG\text{f}(Br\text{)} were obtained from the literature [29], for tert-butanol-water mixtures with a range of co-solvent. Figure 10 depicts the variation of the values of the left hand side of the Equation (36) at 25 °C as a function of mole fraction of the co-solvent from which the differential solvating behavior of different malonate buffer for the initial and transition state is clearly evident. All the values on the left hand side of Equation (36) are negative as found for the aquation of a wide range of cobalt(III) complexes in a mixture of water with different co-solvents [31-33]. In all these cases, the effect of changing solvent structure on the pentacoordinatedcobalt cation in the transition state dominate the effect on the hexacoordinatedcobalt(III) cation in the initial state. Thus, these negative values in the left hand side of Equation (36) indicate that [Co(NH\text{3})\text{]}^3\text{+} is more stable in tert-butanol-water in the presence of malonate buffer than [Co(NH\text{3})\text{]}^3\text{+}Br\text{–}. Moreover, the presence of the malonate buffer in tert-butanol stabilizes the complex more than the free solvent. This is obvious from the more negativity of left hand side of the Equation (36) of malonate media and the free complex.
addition of the medium is suffered from serious changes on the progress constant is non-linear which means that the internal structure of the medium is suffered from serious changes on the progress of tert-butanol to water. As well as, the non-linearity of log γ versus Log [H2O] and the Grumwald-Winstein y-values confirms the differential effect of solvent structures between the initial and the transition states. From the extrathermodynamic correlations, there is marked effect of both solute-solvent and solvent-solvent interactions on the ion-pair formation and aquation reaction. The free energy of activation ΔG° is more or less linearly varied with the mole fraction of tert-butanol indicating of the presence of compensation effect between ΔH° and ΔS°. From the negative values of left hand side of Equation (32), we can conclude that the ions in the transition are more stable than the initial state.

4. Conclusion

In conclusion from all the above discussion, the aquation reaction was accelerated in the presence of malonate buffer due to the formation of ion-pair between the complex cation and the added anion. The plot of log k vs. versus the dielectric constant is non-linear which means that the internal structure of the medium is suffered from serious changes on the progress of tert-butanol to water. As well as, the non-linearity of log γ versus Log [H2O] and the Grumwald-Winstein y-values confirms the differential effect of solvent structures between the initial and the transition states. From the extrathermodynamic correlations, there is marked effect of both solute-solvent and solvent-solvent interactions on the ion-pair formation and aquation reaction. The free energy of activation ΔG° is more or less linearly varied with the mole fraction of tert-butanol indicating of the presence of compensation effect between ΔH° and ΔS°. From the negative values of left hand side of Equation (32), we can conclude that the ions in the transition are more stable than the initial state.

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References