

Research Article

A Characteristic Investigation of Aminocyclohexane-N′-methylurea as a Corrosion Inhibitor for Mild Steel in 1 N H₂SO₄

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The newly synthesized aminocyclohexane-N′-methylurea Mannich base was characterised using FT-IR, H¹NMR, and C¹³NMR spectra and also it was tested as corrosion inhibitor for the mild steel in 1 N sulphuric acid. Inhibitive study of this compound was carried out by weight loss method over the temperature range of 303–333 K, potentiodynamic polarisation, and AC impedance methods. The inhibition efficiency was increased with increasing concentration of inhibitor whereas it was decreased with increasing temperature. Potentiodynamic polarisation study showed that ACMU is a mixed type inhibitor. AC Impedance study reveals that the corrosion of steel was mainly controlled by a charge transfer process. Surface analysis was carried out using SEM technique. The adsorption of inhibitor follows the Tempkin and Langmuir adsorption isotherms. The activation energy (Ea), free energy change (ΔG_ads), enthalpy change (ΔH_ads), and entropy change (ΔS_ads) were calculated to understand the corrosion inhibition mechanism.

1. Introduction

Mild steel is one of the well-known materials used in chemical and allied industries for handling of acids, alkali, and salt solutions. But its susceptibility to corrosion in acid medium is the major obstacles for its larger scale application [1]. Sulphuric acid is mostly employed in chemical industry particularly in pickling process to remove oxide scale from metal surface at elevated temperature [2]. Generally organic compounds are added into the corrosive environment to control the dissolution of metal in acid medium. The corrosion inhibition is mainly decided by the formation of donor-acceptor surface complex between free or π electrons of an inhibitor and vacant d orbitals of the metal atom. A survey of literature reveals that the selection of inhibitor is mostly based upon the type and number of hetero atoms like N, O, and S present in the organic compounds. Many of the available and synthesised organic compounds were used as corrosion inhibitors for mild steel corrosion [1–8], particularly very few newly synthesised Mannich bases were also used as corrosion inhibitor for mild steel corrosion [9].

In the present investigation newly synthesised Mannich base aminocyclohexane-N′-methylurea is tried as a corrosion inhibitor on mild steel corrosion in aqueous sulphuric acid solutions. This compound has one amine group and two amide group which is very essential for an organic compound to behave as an effective corrosion inhibitor. The inhibition efficiency of this compound was studied by weight loss, potentiodynamic polarisation, and AC impedance methods.

2. Experimental Procedure

2.1. Preparation of Specimens. Mild steel specimens of composition Fe = 99.686, Ni = 0.013, Mo = 0.015, Cr = 0.043, S = 0.014, P = 0.009, Si = 0.007, Mn = 0.196, and C = 0.017
were cut to size of 5 cm × 1 cm. The surface of specimens were polished with emery papers ranging from 1/0 to 4/0 grit grades and decreased with trichloroethylene, washed with triply distilled water, and finally dried. Dried specimens were stored in vacuum desiccator containing silica gel. Weight loss measurements were performed as per ASTM method described previously [10].

2.2. Synthesis of ACMU. Aminocyclohexane-N\textsuperscript{1}-methylurea was synthesised by the mannich base reaction of cyclohexylamine, formaldehyde, and urea. Equimolar concentration of cyclohexylamine, formaldehyde, and urea were mixed in the water medium and are stirred vigorously for about three hours. The product was precipitated out as white solid with 80 percent yield. The crude product was purified by column chromatography using chloroform (70%) and methanol (30%) solvent system and then recrystallised using ethanol. The purity of the compound was confirmed by TLC using chloroform: methanol (7:3) eluant. Structure of this compound was confirmed with FT-IR and NMR spectral analysis. The Mannich base reaction is shown in Scheme 1.

2.3. Preparation of Inhibitor Solutions. 0.050 N ACMU in sulphuric acid solution was prepared by dissolving 8.55 g of ACMU in 1000 mL of 1 N sulphuric acid then it was diluted to 0.020, 0.015, 0.010, 0.005, 0.001 N ACMU using 1 N sulphuric acid. These diluted solutions were used as corrosion inhibitor for further studies.

2.4. Structural Elucidation (FT-IR and NMR). The FT-IR spectra were recorded on a JASCO FT-IR 430 spectrophotometer in KBr pellet. The H\textsuperscript{1} NMR and C\textsuperscript{13} NMR spectra were recorded on a Bruker AC 300F (300 MHz) NMR spectrometer using CDCl\textsubscript{3} as solvent and TMS as an internal standard.

2.5. Weight Loss Studies. Weight loss measurements were carried out by weighing the mild steel specimens before and after immersion in the glass vessel containing 100 mL test solution for different time intervals (1 hr, 3 hrs, and 5 hrs) with and without inhibitor. The same procedure was repeated for different temperatures (303 K, 318 K, and 333 K) with one hour immersion period. From the weight loss studies, corrosion rate, inhibition efficiency and surface coverage...
Table I: Inhibition efficiency of ACMU on mild steel corrosion in 1 N H$_2$SO$_4$ at 303 K for various time intervals.

<table>
<thead>
<tr>
<th>Concentration of inhibitor (N)</th>
<th>Corrosion rate (mmpy)</th>
<th>Surface coverage ($\theta$)</th>
<th>Inhibition efficiency (%)</th>
<th>Corrosion rate (mmpy)</th>
<th>Surface coverage ($\theta$)</th>
<th>Inhibition efficiency (%)</th>
<th>Corrosion rate (mmpy)</th>
<th>Surface coverage ($\theta$)</th>
<th>Inhibition efficiency (%)</th>
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<td>—</td>
<td>21.770</td>
<td>—</td>
<td>—</td>
<td>22.736</td>
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<td>—</td>
</tr>
<tr>
<td>0.001</td>
<td>8.470</td>
<td>0.5778</td>
<td>57.78</td>
<td>5.944</td>
<td>0.7270</td>
<td>72.70</td>
<td>4.636</td>
<td>0.7961</td>
<td>79.61</td>
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<td>0.005</td>
<td>6.687</td>
<td>0.6667</td>
<td>66.67</td>
<td>5.052</td>
<td>0.7679</td>
<td>76.79</td>
<td>3.789</td>
<td>0.8333</td>
<td>83.33</td>
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<tr>
<td>0.010</td>
<td>5.795</td>
<td>0.7111</td>
<td>71.11</td>
<td>4.235</td>
<td>0.8055</td>
<td>80.55</td>
<td>3.210</td>
<td>0.8588</td>
<td>85.88</td>
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<tr>
<td>0.015</td>
<td>4.235</td>
<td>0.7889</td>
<td>78.89</td>
<td>3.641</td>
<td>0.8328</td>
<td>83.28</td>
<td>2.407</td>
<td>0.8941</td>
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<tr>
<td>0.020</td>
<td>3.121</td>
<td>0.8444</td>
<td>84.44</td>
<td>2.898</td>
<td>0.8669</td>
<td>86.69</td>
<td>1.649</td>
<td>0.9275</td>
<td>92.75</td>
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</table>
Table 2: Inhibition efficiency of ACMU on mild steel corrosion in 1 N H₂SO₄ at various temperatures.

<table>
<thead>
<tr>
<th>Concentration of inhibitor (N)</th>
<th>Corrosion rate (mmpy)</th>
<th>Surface coverage (θ)</th>
<th>Inhibition efficiency (%)</th>
<th>Corrosion rate (mmpy)</th>
<th>Surface coverage (θ)</th>
<th>Inhibition efficiency (%)</th>
<th>Corrosion rate (mmpy)</th>
<th>Surface coverage (θ)</th>
<th>Inhibition efficiency (%)</th>
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<tr>
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<td>67.539</td>
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<td>8.470</td>
<td>0.5778</td>
<td>57.78</td>
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<td>0.5017</td>
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<td>218.666</td>
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<td>66.67</td>
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<td>60.40</td>
<td>160.266</td>
<td>0.5901</td>
<td>59.01</td>
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<tr>
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<td>5.795</td>
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<td>21.176</td>
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<td>68.65</td>
<td>135.078</td>
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<td>65.45</td>
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<td>0.7889</td>
<td>78.89</td>
<td>17.832</td>
<td>0.7360</td>
<td>73.60</td>
<td>119.029</td>
<td>0.6956</td>
<td>69.56</td>
</tr>
<tr>
<td>0.020</td>
<td>3.121</td>
<td>0.8444</td>
<td>84.44</td>
<td>12.928</td>
<td>0.8086</td>
<td>80.86</td>
<td>107.884</td>
<td>0.7241</td>
<td>72.41</td>
</tr>
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</table>
Table 3: Calculated values of activation energy ($E_a$) and free energy of adsorption ($\Delta G_{ads}$) for mild steel in 1 N $H_2SO_4$ with ACMU.

<table>
<thead>
<tr>
<th>Concentration of ACMU (N)</th>
<th>Energy of activation ($E_a$) KJ/mole</th>
<th>Free energy change ($\Delta G_{ads}$) KJ/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>64.84</td>
<td>103.08</td>
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<tr>
<td>0.001</td>
<td>73.70</td>
<td>109.85</td>
</tr>
<tr>
<td>0.005</td>
<td>74.05</td>
<td>105.10</td>
</tr>
<tr>
<td>0.010</td>
<td>69.21</td>
<td>108.78</td>
</tr>
<tr>
<td>0.015</td>
<td>76.79</td>
<td>111.44</td>
</tr>
<tr>
<td>0.020</td>
<td>75.92</td>
<td>124.55</td>
</tr>
</tbody>
</table>

Table 4: Data obtained from Langmuir adsorption isotherm for mild steel in 1 N sulphuric acid with ACMU in the temperature range of 303–333 K.

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>Free energy change ($\Delta G_{ads}$) KJ/mol</th>
<th>Entropy of adsorption ($\Delta S_{ads}$) J/mol/K</th>
<th>Enthalpy of adsorption ($\Delta H_{ads}$) KJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>−26.34</td>
<td>−13.79</td>
<td>−30.51</td>
</tr>
<tr>
<td>318</td>
<td>−27.64</td>
<td>−9.04</td>
<td>−30.51</td>
</tr>
<tr>
<td>333</td>
<td>−28.94</td>
<td>−4.71</td>
<td>−30.51</td>
</tr>
</tbody>
</table>

2.6. Electrochemical Measurements. The electrochemical measurements were carried out with the conventional three-electrode system. The working electrode was the mild steel of 1 cm$^2$ area and the rest portions are covered with araldite. This working electrode was polished with various grades of emery papers, washed with triply distilled water and degreased with acetone. A rectangular platinum foil of 1 cm$^2$ was used as the counter electrode and saturated calomel electrode (SCE) as reference electrode. All the three electrodes were immersed in 1 N sulphuric acid solution with and without inhibitor. Measurements were performed using CH electrochemical analyser Model CHI 608B instrument. The polarisation measurements were carried out at a scan rate of 2 mV/s and the impedance measurements were carried out in the frequency range of 10 kHz to 0.01 Hz at the open circuit potential. Electrochemical measurements were initiated about 30 min after the working electrode was immersed in solution to stabilize the steady state potential.

2.7. Scanning Electron Microscope (SEM). The mild steel specimens were immersed in 1 N sulphuric acid solution with and without inhibitor for about 24 hours. After the


3. **Results and Discussion**

3.1. **Characterisation of ACMU.** Newly synthesised amino-cyclohexane-N'-methylurea was characterised with data obtained from the FT-IR and NMR spectrum.

3.2. **FT-IR Spectral Analysis.** The FT-IR spectrum of ACMU is shown in Figure 1. A sharp peak at 3400.54 cm\(^{-1}\) is assigned to secondary amine stretching. A double sharp peak at 1550–1650 cm\(^{-1}\) is assigned to the amide group. The sharp peak at 1039 cm\(^{-1}\) is attributed to the cyclohexane ring vibrations.

3.3. **NMR Spectral Analysis**

3.3.1. \(^1\)H-NMR (300 MHz): Solvent CDCl\(_3\). The \(^1\)H-NMR spectrum of ACMU is shown in Figure 2. The multiplet at 1.014–1.285 ppm is assigned to six hydrogen atoms labelled as 1 and 2, multiplet at 1.488–1.905 ppm is assigned to four hydrogen atoms labelled as 3, and multiplet at 2.849 ppm is assigned to one hydrogen atom labelled as 4. The multiplet at 1.81 ppm is assigned to one hydrogen atom labelled as 7, singlet at 1.870 ppm is assigned to two hydrogen atoms labelled as 5, and singlet at 6.184 ppm is assigned for the three hydrogen atoms labelled as 8 and 9.

3.3.2. \(^{13}\)C-NMR (300 MHz): Solvent CDCl\(_3\). The \(^{13}\)C-NMR spectrum of ACMU is shown in Figure 3. The singlet at 25.70 ppm is assigned to two carbon atom labelled as 2, singlet at 26.03 ppm is attributed to one carbon atom labelled as 1, singlet at 29.94 ppm is referred to two carbon atoms labelled as 3, singlet 58.46 ppm is assigned to one carbon atom labelled as 5, singlet at 68.29 ppm is assigned to one carbon atom labelled as 6, and singlet at 150.6 ppm is assigned to one carbon atom labelled as 6.

The proposed ACMU structure based upon the FT-IR, \(^1\)H-NMR, and \(^{13}\)C-NMR spectrum is shown in Figure 4.

3.4. **Weight Loss Studies.** Each weight loss studies was repeated three times and also its standard deviation was calculated. The standard deviation was various between 0.5 and
2.1. Table 1 shows the value of inhibition efficiency, surface coverage, and corrosion rate for various concentration of inhibitor in 1 N Sulphuric acid for the period of 1 hr, 3 hrs and 5 hrs. The addition of inhibitor to acid decreases the corrosion rate due to the adsorption of inhibitor on mild steel surface. The inhibition efficiency was found to be increased with increasing time and concentration of inhibitor. The maximum inhibition efficiency was found to be 92.75% in 1 N sulphuric acid for 0.02 N ACMU at 5 hrs.

Table 2 shows the value of inhibition efficiency, surface coverage, and corrosion rate for various concentration of inhibitor in 1 N sulphuric acid for a period of 1 hr at various temperatures. The inhibition efficiency was found to be increased with increasing concentration of inhibitor and decreased with increasing temperature. This efficiency was explained as follows: the inhibitor adsorbed on to the metal surface, and an increase in temperature resulted in desorption of some adsorbed molecules, leading to a decrease in inhibition efficiency [11]. The maximum inhibition efficiency was found to be 84.4% in 1 N sulphuric acid for 0.020 N ACMU at 300 K.

**Thermodynamic/kinetic consideration.** Adsorption behaviour of ACMU on mild steel surface was very much essential to understand the corrosion inhibition mechanism. Temkin and Langmuir adsorption isotherms were tested by plotting \( \log C_{\text{inh}} \) versus surface coverage (\( \theta \)) and \( C_{\text{inh}}/\theta \) versus \( C_{\text{inh}} \) respectively. Both plots gives straight line confirming inhibition of ACMU on mild steel corrosion in 1 N sulphuric acid obeys Temkin and Langmuir adsorption isotherm which is shown in Figures 5 and 6. This result reveals that the adsorption of ACMU on mild steel is mono layered. Langmuir adsorption isotherm is given in (4):

\[
\frac{C_{\text{inh}}}{\theta} = \frac{1}{k_{\text{ads}}} + C_{\text{inh}}, \quad (4)
\]

where \( C_{\text{inh}} \) is the inhibitor concentration and \( k_{\text{ads}} \) is the equilibrium constant and \( \theta \) is the degree of surface coverage of the inhibitor.

\( k_{\text{ads}} \) was calculated from the intercept of the straight line obtained in Langmuir adsorption isotherm. The Energy of activation and free energy of adsorption were calculated using (5):

\[
\log \frac{P_2}{P_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right], \quad (5)
\]

\[\Delta G_{\text{ads}} = -RT \ln (55.5 k).\]

Equilibrium constant \( k_{\text{ads}} \) for various concentration of inhibitor was calculated by using (6).

\[k_{\text{ads}} = \frac{\theta}{C (1 - \theta)}, \quad (6)\]

where \( P_1 \) and \( P_2 \) are the corrosion rate at temperature \( T_1 \) and \( T_2 \), respectively, \( \theta \) is the surface coverage, \( C \) is the concentration of inhibitor, and \( k_{\text{ads}} \) is the equilibrium constant.

Calculated values of activation energy (\( E_a \)) and free energy of absorption (\( \Delta G_{\text{ads}} \)) were given in Tables 3 and 4. Greater values of activation energy for the inhibited system over the uninhibited system suggested that the adsorption is physisorption. The negative value of \( \Delta G_{\text{ads}} \) indicated the spontaneous adsorption of ACMU inhibitor on the mild steel surface and also there was strong interaction between inhibitor molecule and the mild steel surface [12]. Generally the values of \( \Delta G_{\text{ads}} \) up to \(-20\ KJ/mole\) are consistent with physisorption, while those around \(-40\ KJ/mole\) or higher are associated with chemisorptions [13]. The calculated \( \Delta G_{\text{ads}} \) values were around \(-20\ KJ/mole\) indicated that the adsorption mechanism of ACMU on mild steel in 1 N sulphuric acid at the studied temperature was physisorption [14].

Thermodynamically \( \Delta G_{\text{ads}} \) was related with entropy of adsorption and enthalpy of adsorption process via (7):

\[\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S_{\text{ads}}. \quad (7)\]

The Langmuir adsorption isotherm however can be expressed by (8) [12]:

\[
\log \frac{\theta}{1-\theta} = \log A + \log C_{\text{inh}} - \frac{Q_{\text{ads}}}{2.303RT}, \quad (8)
\]

where \( A \) is the constant, \( Q_{\text{ads}} \) is the heat of adsorption equal to enthalpy of adsorption \( \Delta H_{\text{ads}} \). If \( \log (\theta/1-\theta) \) is plotted against \( 1000/T \) at various concentrations, the slope of the straight line was \(-\Delta H_{\text{ads}}/2.303R\). The negative value of \( \Delta H_{\text{ads}} \) is indicated that the adsorption of ACMU onto the mild steel surface was exothermic. In the exothermic process physisorption was distinguished from chemisorption by considering the absolute value of \( \Delta H_{\text{ads}} \). For physisorption, absolute value \( \Delta H_{\text{ads}} \) is lower than 40 KJ/mol, while for chemisorptions, it is around 100 KJ/mol [11]. Calculated values of \( \Delta H_{\text{ads}} \) are lower than 40 KJ/mol therefore adsorption of ACMU on mild steel in 1 N sulphuric acid is physisorption.

The negative value of \( \Delta S_{\text{ads}} \) indicated that inhibitor molecules freely moving in the bulk solution and adsorbed...
3.5. Potentiodynamic Polarisation Studies. Polarisation curves of mild steel electrode in 1 N sulphuric acid with and without ACMU at 303 K are shown in Figure 7. The anodic Tafel slope and the cathodic Tafel slope were changed with concentration, which indicated that the inhibitor controls both the reactions [17].

It can be seen from the Table 5 that the \( I_{corr} \) values were decreased with increasing concentration of inhibitor. A compound could be classified as cathodic or anodic type inhibitor when the change of \( E_{corr} \) is larger than 85 mV [18]. Since the largest displacement shown by the ACMU was 14 mV, it could be concluded that the molecule is mixed type inhibitor [18]. The maximum inhibition efficiency of the ACMU inhibitor was found to be 89.03% in 1 N sulphuric acid for 0.020 N ACMU. Inhibition efficiency obtained from the polarisation method was in good agreement with weight loss studies.

3.6. AC Impedance Studies. Figure 8 shows the impedance diagram of mild steel in 1 N sulphuric acid with and without inhibitor. Impedance parameters derived from Nyquist plots were given in Table 6. It was observed that the value of charge transfer resistance (\( R_{ct} \)) increased with increase in concentration of inhibitor. On the other hand, the value of double layer capacitance (\( C_{dl} \)) decreased with increase in inhibitor concentration. This is due to the increase in surface coverage of the inhibitor. The inhibition efficiency of the inhibitor is increased with increase in concentration of inhibitor. The maximum inhibition efficiency was found to be 95.03% in 1 N sulphuric acid for 0.02 N ACMU. As impedance diagram for solutions examined have almost a semicircular appearance, it indicates that the corrosion of mild steel is mainly controlled by a charge transfer process [18]. Inhibition efficiency obtained from AC impedance method was good agreement with polarisation and weight loss studies.

3.7. Scanning Electron Micrograph. Surface analysis was carried out by SEM technique in order to evaluate the surface conditions of the mild steel in contact with 1 N sulphuric acid solution. The micrographs of the mild steel surface in the presence of 1 N sulphuric acid with and without ACMU inhibitor are shown in Figures 9(a) and 9(b). In the absence of inhibitor the surface was covered with a high density of pits. In the presence of the inhibitor the micrograph shows no evidence of pitting but shows a smooth surface. This result is due to the adsorption of inhibitor molecules around the pits. This passive film blocks the active sites present on the mild steel surface [19].

4. Conclusions

The following conclusions were made from the study.

(i) Inhibition efficiency of the newly synthesised ACMU was increased with increasing concentration of inhibitor and time and decreased with temperature.
(ii) The maximum inhibition efficiency observed in weight loss method was 92.75% in 1 N sulphuric acid for 0.02 N ACMU at 303 K.

(iii) The negative value of $\Delta G_{\text{ads}}$ indicated that the adsorption is spontaneous.

(iv) The negative value of $\Delta H_{\text{ads}}$ indicated that the adsorption is exothermic.

(v) Free energy of adsorption and Enthalpy of adsorption values shows the adsorption process is physisorption.

(vi) ACMU follows Tempkin and Langmuir adsorption isotherm.

(vii) ACMU behaves as mixed type inhibitor.

(viii) The maximum inhibition efficiency obtained in polarisation method was 89.03% in 1 N sulphuric acid for 0.02 N ACMU at 303 K.

(ix) AC impedance experiments indicated that the corrosion of mild steel in 1 N sulphuric acid with ACMU was mainly controlled by charge transfer process.

(x) The maximum inhibition efficiency obtained in AC impedance method was 95.03% in 1 N sulphuric acid for 0.02 N ACMU at 303 K.

(xi) Inhibition efficiency obtained in AC impedance and potentiodynamic polarisation methods were in good agreement with conventional weight loss method.

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References


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