Studies on Basic Properties of the Bis (eugenolato) – Zinc (II)**

—X-ray, Thermal Analysis, Solubility in Acid-Alkali Solution and Specific Gravity—

by

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1. Introduction

For the purpose to examine the basic properties of zinc oxide-eugenol cement, the authors, synthesizing bis(eugenolato)-zinc(II) (zinc eugenolate), performed IR and elemental analyses on it. As a result, the authors found the optimum synthesizing method. That is, a high yield of bis(eugenolato)-zinc(II) could be available by making sodium eugenolate react with zinc chloride at room temperature, with methanol used as a solvent. At the same time, from the results of elementary analysis and IR-measurement, the authors presumed that the product was a chelate compound of 1 mol zinc and 2 mol eugenol, of Zn-centered five-membered ring structure. It was also made out that the synthesized crystal was of column-like or needle-like shape, 10–40 μ in size, and slightly soluble or insoluble in water and in various kinds of organic solvents.

Then, the authors, for further examination on the properties of bis(eugenolato)-zinc(II), perform X-ray diffraction and differential thermal analysis, and examines its stability to acid-alkali solution and its specific gravity.

2. Experimental Methods

(1) Material: bis(eugenolato)-zinc(II), synthesized in the previous report (1) is used.

(2) Measurement

1) X-ray diffraction: Rigaku Denki Sha’s X-ray diffraction apparatus is used. The measuring conditions are as follows: target: Cu, filter: Ni, 40 KV, 30 mA, chart speed: 20 mm/min., time constant: 10 sec, scanning speed: 20°/min.

2) Differential thermal analysis: Rigaku Denki Sha’s differential thermobalance (TG-DTA) is used. Thermocouple: Rt.Ph 13%-Pt Vessel: of platinum, 5.5 mm φ, temperature-rising velocity: 5°C/min.

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3) **Solubility in acid-alkali solution:** HCl is used as acid solution, and NH₄OH as alkali solution. As shown in Table 1, solutions with pH values respectively 3.0, 5.0, 9.0 and 11.0 are prepared, and 50 ml of each is used. As pH 7 solution, distilled water is used after being boiled.

0.4000 g of specimen, accurately measured, is added to each 50 ml of solution to be shaked for respectively 1, 24 and 72 hours in the sealed vessel. Then, the solution is filtrated, and Zn^{++} is determined by the atomic absorption spectrometer, SAS 275, Daini Seiko Sha made. The analysis conditions are as follows: Wave length of Zn, 2138Å; Lamp current, 8 mA; Slit width, 0.3 mm; Voltage, 270 V; Burner height, 4.0 mm, Air flow rate, 1.9 kg/min. Measurement is performed three times to obtain an average value.

4) **Specific gravity:** Specific gravity is measured, using a Hubbard type specific gravity bottle, with pure methanol used as a solvent.

### 3. Experimental Results and Discussion

1) **X-ray diffraction**

Fig. 1 shows the X-ray diffraction pattern of bis(eugenolato)-zinc(II) synthesized. (II) is the diffraction pattern shown by COPELAND, et al.[2].

As shown here, in the case of the synthesized material, high peaks appear at 2θ = 10.6°, 13.0°, 18.3° and 27.5°, and then comparatively low peaks at 19.6°, 20.0°, 22.7° and 30.2°. While, the diffraction pattern shown by COPELAND, et al., almost coincident with the authors', shows a very high peak at 2θ = 5.0°, whose attribution is not traceable.

2) **Differential thermal analysis**

Fig. 2 shows the TG-DTA curves of bis(eugenolato)-zinc(II) synthesized.

As shown here, TG, decreasing at around 150°C, shows approximately 75% of weight loss at 350°C, and 78.79% at 800°C.

While, DTA curve shows an exothermic phenomenon at around 330°C, and then a small endothermic phenomenon at 550°C. That is, the decomposition of bis(eugenolato)-zinc(II) begins at around 150°C and almost finishes at around 350°C. The decomposition residue at 800°C is 21.21%. Supposing bis(eugenolate)-zinc(II) is a chelate compound formed by the interaction of 1 mol Zn and 2 mol eugenol, it being decomposed by heating, zinc would become zinc oxide. On this supposition, the authors calculate its weight loss to find the calculated value is almost coincident with the

<table>
<thead>
<tr>
<th>pH level</th>
<th>Adjustment of buffered solution</th>
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<tbody>
<tr>
<td>3.0</td>
<td>Distilled water 151.5 ml + 1 M sodium acetate 15 ml + 1 N HCl 48.5 ml</td>
</tr>
<tr>
<td>5.0</td>
<td>Distilled water 190.0 ml + 1 M sodium acetate 40 ml + 1 N HCl 10.0 ml</td>
</tr>
<tr>
<td>7.0</td>
<td>Distilled water, after being boiled</td>
</tr>
<tr>
<td>9.0</td>
<td>0.1 M NH₄Cl 10 ml + 0.1 N NH₃OH 2 ml</td>
</tr>
<tr>
<td>11.0</td>
<td>0.1 M NH₄Cl 10 ml + 0.1 N NH₃OH 64 ml</td>
</tr>
</tbody>
</table>

Table 1. Adjustment of buffered solution
theoretical value, with 0.33% difference. From the facts shown above, it is proved that bis(eugenolato)-zinc (II) is a compound of 1 mol Zn and 2 mol eugenol.

3) Solubility in acid-alkali solution

Figs. 3, 4 and 5 show the solubility of bis(eugenolato)-zinc (II) in acid-alkali solution, respectively after 1, 24 and 72 hours.

As shown here, solubility varies to a great degree in accordance with the change of pH. That is, solubility after 1 hour shows about 97% at pH 3.0, 0.02% at pH 7.0, and 0.11 and 0.25% at pH 9.0 and 10.0 respectively. Similarly, after 24 hours, it shows
Fig. 3. Solubility in acid-alkali solution of bis (eugenolato)-zinc (II) (1hr)

Fig. 4. Solubility in acid-alkali solution of bis (eugenolato)-zinc (II) (24hr)
a large value of 98.19% at pH 3.0, then 66.84 and 0.12% at pH 5.0 and 7.0, and 0.19% at pH 11.0. Again, after 72 hours, solubility becoming large in every case, shows 98.35% at pH 3.0, 95.15 and 0.10% at pH 5.0 and 7.0, and 0.19% at pH 9.0 and 11.0.

From the results shown above, it is made out that bis(eugenolato)-zinc(II) is very soluble in the range of pH lower than 5.0, but comparatively stable in alkaline range higher than pH 7.0. Especially it shows very small values at pH 7.0.

Though the solubility of zinc oxide-eugenol cement is generally considered due to zinc oxide and addition materials being soluble, bis(eugenolato)-zinc(II) shows comparatively high solubility in the acid range, while it is also slightly soluble at around pH 7.0, as proved in the present studies. From the facts shown above, it is presumed that the solubility of zinc oxide eugenol cement can not easily be lowered.

4) Specific gravity
It is proved that the specific gravity of bis(eugenolato)-zinc(II) is 1.47, comparatively a large value.

5. Conclusions
The results of the present experiments can be itemized as follows:

1) High peaks of X-ray diffraction of the synthesized bis(eugenolato)-zinc(II) appear at $2\theta = 10.6, 13.0, 18.3$ and $27.5^\circ$. These peaks coincide with those shown by Copeland, et al.

2) The decomposition of the synthesized bis(eugenolato)-zinc(II) begins at around 150°C and its weight loss reaches 78.79% at 800°C. On the other hand, DTA becomes exothermic at 330°C and endothermic at 550°C.
3) The synthesized product proves to be a compound of 1 mol of Zn and 2 mol of eugenol, judged by the amount of zinc oxide calculated from the decomposition residue.

4) The synthesized product has comparatively large solubility in the acid solution, while its solubility becomes small at pH 7.0 and in the alkaline range, showing 0.02 and 0.11\% at pH 7.0 and 9.0 respectively after 1 hour.

5) The specific gravity of the synthesized product is 1.47.

References
