Complexes of Metallochromic Substances. X*

High-Sensitive and Selective Determination of Copper by means of Aminomethylazo III

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Summary. Aminomethylazo III, i.e. 2.7-bis[o-di(carboxymethyl)aminomethylphenylazo]chromotropic acid, was found to be a high-sensitive and selective reagent for the spectrophotometric copper determination. The relative molar absorptivity for copper is 75,000 cm²mM⁻¹. The method described is advantageous for the determination of trace amounts of copper in uranium. The composition and stability constants of the copper(II) complexes formed, and the dissociation constants of Aminomethylazo III were determined.

Aminomethylazo III is the trivial name given to the 2.7-bis-[o-di(carboxymethyl)aminomethylphenylazo]-chromotropic acid, see Formula I, obtained by coupling of diazotized o-aminobenzyliminodiacetic acid with chromotropic acid⁴, ⁵. It is one of the type of ortho-substituted 2.7-bisazochromotropic acids, which are known as excellent metallochromic reagents in spectrophotometry.

Aminomethylazo III gives a perceptible metallochromic effect with many metal ions, but only its reaction with copper(II) ions is of practical importance.

Experimental
1.00·10⁻⁴ m solution of Aminomethylazo III (mol. weight 818.8; the synthesis and analytical control see⁴,⁵), and 2.00·10⁻⁴ m solutions of metal nitrates were prepared as usual. The aqueous solutions of Aminomethylazo III are stable for some months. The NTA-phosphate-acetate buffer (its composition see ⁶) was used for pH-adjustments in measurements of proton complexes formation. The pH-adjustment for the formation of metal complexes was carried out with non-complexing solutions (their composition see ⁶). The exact pH values of these solutions were controlled simultaneously. All chemicals used were "pro analysi" products of Lachema, Brno. The constants were determined at the constant ionic strength of 0.20 n (potassium nitrate).

The pH-adjustment was controlled potentiometrically by using the pH-meter "Modell E 187", Metrohm A.G., Herisau (Switzerland), with the combined glass-

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silver-silver(I) chloride electrode. The Soviet instrument SF-4 and the English instrument Unicam SP-700, with 1.00 cm quartz cuvettes, were used for the spectrophotometric measurements.

Results and Discussion

Proton Complexes of Aminomethylazo III

The dissociation constants of the Aminomethylazo III proton complexes were determined spectrophotometrically by a method described earlier\(^3\). They are given in Table 1.

Table 1. Dissociation Constants of Aminomethylazo III Proton Complexes

<table>
<thead>
<tr>
<th>n</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>(pK_n^*)</td>
<td>14.1</td>
<td>13.3</td>
<td>12.2</td>
<td>10.3</td>
<td>9.3</td>
<td>6.3</td>
<td>4.9</td>
<td>3.8</td>
<td>2.9</td>
<td>1.3</td>
<td>-1.0</td>
<td>-3.3</td>
</tr>
</tbody>
</table>

\(K_n = [LH_n-1][H]/[LH_n]\).

The dissociation of the both phenolic groups is expressed by the constants \(K_1\) and \(K_2\), and is accompanied by a colour change from red into blue. The protonization of the carboxyl anions is expressed by the constants \(K_3 - K_6\) and is without perceptible colour effect. The constants \(K_7 - K_{10}\) correspond probably to the protonization of the aminomethyl groups, and the sulphonic anion groups. The determination of the first protonized groups is very difficult in this case. The last constants \(K_{11}\) and \(K_{12}\) correspond to the protonization of the both azo groups, which is connected with a colour change from red into green.

The \(\alpha_H\)-pH dependence and its differential form (see\(^1\)) are given in Fig. 1.

Reactions of Aminomethylazo III with Metal Ions

Aminomethylazo III gives complexes with many metal ions, but this complex formation is connected with a relative low metallochromic sensitivity in almost all cases. The relative molar absorptivities for metal ions in these reactions at optimal pH-conditions are given in Table 2.