A Novel Aluminum (III)-selective PVC Membrane Electrode Based on a Schiff Base Complex of bis(5-sulphonate salicylaldehyde) 2,3-diaminobenzene

Hui Yao*, Shuai Wang, Xiaoqian Ma, Ling Ren, Feng Yan

College of Applied Chemistry, Shenyang University of Chemical Technology, 11# Street Shenyang Economic & Technology Development Area, 110142, Shenyang, China
*E-mail: yaohui_syuct@163.com

Received: 25 November 2013 / Accepted: 6 January 2014 / Published: 2 February 2014

A schiff base complex bis(5-sulphonate salicylaldehyde) 2,3-diaminobenzene (SSDA) was synthesized, which was used as ionophore in aluminum poly(vinyl chloride) matrix membrane selective electrode. The proposed electrode, with optimum composition, exhibited an excellent near-Nernstian response for Al$^{3+}$ over a wide concentration range of 1.0×10$^{-5}$~0.15 mol/L with a slope of 15.6mV per decade and a detection limit of 5.1×10$^{-6}$ mol/L in pH 3.5-4.5 salt solution at 25°C. It showed good selectivity towards Al$^{3+}$ ion, a relatively fast response time and long life time, and good reproducibility. The operational pH range of the proposed electrode was 3.5–4.5. The response mechanism was discussed in view of the coordination theory and UV–visible spectroscopy. In addition, the proposed electrode was applied for the determination of Al$^{3+}$ ion in food products successfully.

Keywords: schiff base, bis(5-sulphonate salicylaldehyde) 2,3-diaminobenzene , ion selective electrode, aluminum, PVC, ionophore

1. INTRODUCTION

Aluminum is one of the richest elements in earth rocks and soil mineral, which ranks third after oxygen and silicon. It is widely used in architecture, transport, household appliances, machinery, electronics and telecommunication, and as a flocculating agent in potable water treatment units [1-3]. However, with the development of science and technology and the improvement of people’s living standard, the harmful aspect of aluminum is also recognized gradually. Many recent studies have shown that increased deposition in bone and the central nervous system can cause neurotoxicity in high
dosage, which can alter the function of blood–brain barrier. It plays a significant role in the pathology of Parkinson’s disease (PD), Alzheimer’s disease (AD) and diseases of dialysis [4-6]. Consequently, the need of determination for aluminum in environment, medicine, foodstuff, etc. is increasing. Nowadays, there have many common methods to monitor the trace amount of aluminum in real sample. Such as flow injection analysis (FIA) [7], graphite furnace atomic absorption spectrometry (GFAAS) [8,9], inductively coupled plasma atomic emission spectrometry (ICP-AES) [10], etc. However, these methods require expertise and infrastructure backup. Thus, it is great significant to develop a convenient, fast technology to determine the amount of aluminum.

Ion selective electrode with its excellent features is widely used to determine many elements in real sample. Ion selective electrode includes many parts, in which the neutral carrier is playing the most important role. Due to the special selectivity between the ionophore and the element, ion selective electrode have potential response characteristics, including wide linear range, low detection limit, fast response time, good selectivity, etc [11-13].

A crucial role in the ion-selective membrane is played by the ionophore, which provides selective ion binding. Recently, there are some membrane sensors have been reported for Al$^{3+}$[14-20], but there is a constant need to develop novel selective ionophores that improve selectivity of ISEs. In this work, we were also motivated to investigate the fabrication and characterization of a new ISE based on schiff base complex, bis (5- sulphonate salicylaldehyde) 2, 3- diaminobenzene(SSDA)(Fig. 1), as a suitable ionophore. The results show that the proposed electrode exhibits good selectivity with a wide linear range and low detection limit for Al$^{3+}$ ion, and has been preliminary applied in the detection of Al$^{3+}$ ion in real samples.

2. EXPERIMENT

2.1. Apparatus and reagents

All potential measurements were carried out with a digital pH/mV meter (pHS-25) at laboratory ambient temperature. Fourier transform infrared (FTIR) spectra by KBr pellets were obtained on a FT-IR 470 spectrometer (Nicolet) at room temperature. UV-vis absorption spectra were obtained with UV-3100 spectrophotometer (SHI-MADZU) at room temperature. NMR spectra were obtained with Mercury 300 (Varian).

All reagents used were of analytical grade. High molecular weight poly (vinylchloride) (PVC), Salicylaldehyde, O-phenylenediamine, Tetrahydrofuran (THF), dibuthylphthalate (DBP), dioctylphthalate (DOP), tributyl phosphate (TBP), diethyl phthalate (DEP) and all kinds of salts were all purchased from Sinopharm Chemical Reagent Co., Ltd (Shenyang, China). All aqueous solutions were prepared with deionized distilled water.

2.2. Synthesis of ionophore

The synthesis of ionophore was divided into two steps: firstly, the intermediate product 5-sulphonate salicylaldehyde was synthesized according to procedure previously described [14]. Next,
the ionophore schiff base complex of bis(5-sulphonate salicylaldehyde) 2,3-diaminobenzene (SSDA) was synthesized as follow: 1mmol of o-Phenylenediamine and 2mmol 5-sulphonate salicylaldehyde were condensed by refluxing in 70 mL of absolute ethanol for 1h. The solution was left at room temperature. SSDA was obtained as yellow microcrystals which filtered and washed with 10 mL of absolute ethanol and then recrystallized from ethanol–chloroform (1:3 v/v). The characteristics of product are as follow:

$^{1}H$-NMR (CDCl$_3$, 300MHz): $\delta=8.4$ (s, 2H, -HC=N), 6.9~7.8 (m, 6H, Ar-H).
IR (KBr): $\gamma$/cm$^{-1}$: 3460(-OH), 1625(C=N).

2.3. Preparation of electrode

The membrane components 5mg SSDA, 66mg plasticizer (DOP), 300mg PVC were mixed and dissolved in 5mL THF, with constantly stirring. The resulting uniform and viscous solvent was poured into a glass dish of 25mm diameter. THF was allowed to evaporate slowly at room temperature until a transparent PVC membranes were obtained with an average thickness of 0.5mm. After 24h, a 10mm (approximately) diameter piece was cut and mounted on the ground end of the Pyrex tube. The tube with the membrane was then filled with internal solution of $1.0\times10^{-2}$ mol/L Al$^{3+}$ and 1.0 mol/L NaCl. A silver/silver chloride electrode was used as an internal reference electrode. The sensor was finally conditioned for 24h by soaking in $1.0\times10^{-2}$ mol/L Al$^{3+}$ solution, rinsed well with distilled water and stored in air when not in use. All the potential measurements were carried out by using the following cell assembly:
3. RESULT AND DISCUSSION

3.1. Response mechanism of Electrode

Schiff base (SSDA) was employed as aluminum selective ionophore in the preparation of aluminum ion-selective electrode. This Schiff base was selected due to its special ring structure, which included two \( \text{–C}=\text{N} \) groups and two \( \text{–OH} \) groups. Because the lone pair electrons were belonged to both oxygen and nitrogen, a more stable coordination compound could be easily obtained by the coordination between \( \text{Al}^{3+} \) which had empty orbit and Schiff base ionophore which had lone pair electrons. So these two ring-conjugated structures in rich ion situation were expected to improve the electrode response performance. The coordination mechanism of \( \text{Al}^{3+} \) and schiff base ionophore was showed in the Fig.2.

![Figure 2. Cooperation mechanism of aluminum(III)ion and bis(5-sulphonate salicylaldehyde) 2,3-diaminobenzene](image)

To confirm the coordination reaction between the ionophore and \( \text{Al}^{3+} \) ions, the UV-visible spectroscopic experiments were carried out and the result is shown in Fig.3. It is seen that the maximum absorption wavelength of schiff base ionophore (a) is at wavelength 410nm. After coordination between ionophore and \( \text{Al}^{3+} \) ions, the maximum absorption wavelength increase to 458nm. Thus change indicates the complexation of schiff base with \( \text{Al}^{3+} \) ions.
3.2. Optimization of membrane composition

The selectivity, sensitivity and linearity of ion selective electrode largely depend on the membrane composition and the properties of plasticizer. In order to obtain the best potential response performance of the electrode, the effect of different amounts of the components and different kinds of plasticizer were studied [15].

The plasticizer to be used in membrane should exhibit high lipophilicity, have high molecular weight, low tendency for exudation from the polymer matrix, low vapor pressure and high capacity to dissolve the substrate and other additives present in the membrane. Additionally, its viscosity and dielectric constant should be adequate. The nature of plasticizer also influences the mobility of the ionophore molecule, the state of ligand and hence, the response characteristics [16-17].

Thus, the potential response of four kinds of aluminum selective electrodes which were made with different plasticizers (TBP, DOP, DBP, and DEP) was shown in Fig.4. It indicated that the aluminum selective electrode with DOP has better behavior than the others with a good Nernstian response over a wide linear range (1.0×10⁻⁵ to 0.15 mol/L). So DOP was used to fabricate aluminum selective electrode.
It's well known that the potential response characteristics of the electrode also depend significantly on the membrane composition [18-20]. Therefore, the performance characteristics, measurement concentration ranges, slope of the calibration curve, detection limit were examined with several membranes having ingredients of different proportions (as listed in Table 1). Potential response characteristics of all different electrodes were studied in the concentration range of $1.0 \times 10^{-7} - 1.0 \times 10^{-1}$ mol/L Al$^{3+}$ ion solutions, with pH 3.5-4.5. It is clear that No.4 electrode containing w(ionophore) 15mg, w(PVC) 350mg and w(DOP) 660mg displayed excellent potential response characteristics towards Al$^{3+}$ ion ranging from $1.0 \times 10^{-5}$ to $1.0 \times 10^{-1}$ mol/L, with a detection limit of $5.1 \times 10^{-6}$ mol/L and a slope of 15.6 mV/dec. And this electrode was chosen for further studies.

**Table 1.** Optimization of the membrane ingredients

<table>
<thead>
<tr>
<th>Sensor No.</th>
<th>PVC (mg)</th>
<th>Ionophore (mg)</th>
<th>DOP (mg)</th>
<th>Working activity range (mol/L)</th>
<th>Slope (mV/dec.)</th>
<th>R</th>
<th>Detection limit(mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>300</td>
<td>10</td>
<td>660</td>
<td>$1.0 \times 10^{-7}$ to $1.0 \times 10^{-1}$</td>
<td>13.5</td>
<td>0.9868</td>
<td>$8.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>2</td>
<td>350</td>
<td>10</td>
<td>600</td>
<td>$1.0 \times 10^{-5}$ to $1.0 \times 10^{-2}$</td>
<td>14.3</td>
<td>0.9767</td>
<td>$6.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>3</td>
<td>400</td>
<td>10</td>
<td>550</td>
<td>$1.0 \times 10^{-3}$ to $1.0 \times 10^{-1}$</td>
<td>14.7</td>
<td>0.9937</td>
<td>$3.3 \times 10^{-6}$</td>
</tr>
<tr>
<td>4</td>
<td>350</td>
<td>15</td>
<td>660</td>
<td>$1.0 \times 10^{-7}$ to $1.5 \times 10^{-1}$</td>
<td>15.6</td>
<td>0.9992</td>
<td>$5.1 \times 10^{-6}$</td>
</tr>
<tr>
<td>5</td>
<td>400</td>
<td>15</td>
<td>600</td>
<td>$1.0 \times 10^{-5}$ to $2.0 \times 10^{-2}$</td>
<td>17.1</td>
<td>0.9910</td>
<td>$6.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>6</td>
<td>300</td>
<td>15</td>
<td>550</td>
<td>$1.0 \times 10^{-3}$ to $1.0 \times 10^{-2}$</td>
<td>16.8</td>
<td>0.9902</td>
<td>$6.8 \times 10^{-6}$</td>
</tr>
<tr>
<td>7</td>
<td>400</td>
<td>30</td>
<td>660</td>
<td>$1.0 \times 10^{-7}$ to $1.0 \times 10^{-1}$</td>
<td>15.1</td>
<td>0.9898</td>
<td>$7.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>8</td>
<td>300</td>
<td>30</td>
<td>600</td>
<td>$1.0 \times 10^{-5}$ to $1.0 \times 10^{-2}$</td>
<td>16.2</td>
<td>0.9900</td>
<td>$8.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>9</td>
<td>350</td>
<td>30</td>
<td>550</td>
<td>$1.0 \times 10^{-5}$ to $1.0 \times 10^{-2}$</td>
<td>18.8</td>
<td>0.9899</td>
<td>$7.5 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
3.3. Effect of pH and the concentration of internal solution on the response of the electrode

The performance of the electrode was also investigated at different pH values. The effect of pH on membrane electrode was examined over the pH range of 3–5 at Al\(^{3+}\) ion concentration of 1.0×10\(^{-3}\)mol/L to 1.0×10\(^{-2}\) mol/L. The results are shown in Fig.5. As can be seen, the potentials remain constant in the pH range 3.5- 4.5. At pH values lower than 3.5, the pH of solution also affected the potential response. This is probably due to partial destruction of zeolite lattice, which occurs in acidic media,[21] and also simultaneous response of the electrode to positively charged H\(_3\)O\(^+\) and Al\(^{3+}\) ions. While the observed increase in potential at higher pH values could be attributed to the formation of some aluminum hydroxide species.

![Figure 5. Effect of pH on the potential response of the aluminum ion-selective electrode at different Al\(^{3+}\) concentrations: (●) 1.0×10\(^{-3}\) mol/L and (■) 1.0×10\(^{-2}\) mol/L.](image)

The performance of the proposed electrode in relation to the variation in concentration of internal solution of Al\(^{3+}\) was explored (from 1.0×10\(^{-3}\) mol/L to 1.0×10\(^{-1}\) mol/L) and the potential response of the Al\(^{3+}\) ion-selective electrode was obtained. It was found that the best performance of potential response was exhibited in the internal solution with 1.0×10\(^{-2}\) mol/L, which shown in the Fig.6.
Figure 6. Effect of internal solution concentration on the aluminum selective electrode: (■) 1.0×10⁻¹ mol/L, (●) 1.0×10⁻² mol/L and (▼) 1.0×10⁻³ mol/L.

3.4. Performance test of aluminum ion-selective electrode

3.4.1 Calibration curve of aluminum ion-selective electrode

The calibration curve of aluminum selective electrode was obtained in the working concentration range of 1.0×10⁻¹ mol/L and 1.0×10⁻⁶ mol/L Al³⁺ solution, with pH 3.5-4.5 and 1.0×10⁻³ mol/L and 1.0×10⁻¹ mol/L of internal solution concentration at 25°C. The results thus obtained indicate that the proposed aluminum electrode exhibits Nernstian slope (15.6mv/dec) over a wide concentration range of 1.0×10⁻⁵–1.0×10⁻¹ mol/L. The detection limit, defined as the concentration of aluminum ion obtained when extrapolating the linear range of calibration curve to the base line potential is 5.1×10⁻⁶ mol/L.
3.4.2 The selectivity of aluminum selective electrode

Table 2. Selectivity coefficients $K_{i,j}$ of various interfering ions

<table>
<thead>
<tr>
<th>Interfering Ion (0.1mol/L)</th>
<th>$K_{i,j}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{2+}$</td>
<td>0.045</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>0.085</td>
</tr>
<tr>
<td>F$^-$</td>
<td>0.144</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>0.037</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>0.045</td>
</tr>
<tr>
<td>PO$_4^{3-}$</td>
<td>0.007</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>0.007</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>0.029</td>
</tr>
</tbody>
</table>

The selectivity is the most important characteristics as it determines the extent of utility of a sensor in real sample measurement. The selectivity coefficients for the selective membrane electrode were measured by the fixed interference method (FIM) [22-25]. In the method, the potential response
of a cell comprising an ion-selective electrode and a reference electrode is measured for solutions of constant activity of the interfering ion, \(a_i\), and varying activity of the primary ion, \(a_j\). The potential values obtained are plotted vs. the logarithm of the activity of the primary ion. The intersection of the extrapolated linear portions of this plot indicates the value of \(a_i\) that is to be used to calculate \(K_{ij}\) from the following equation: 
\[
K_{ij} = a_i / (a_j)^{z_i/z_j}
\]
where both \(z_i\) and \(z_j\) have the same sign (positive). The selectivity coefficient of various interfering ions \(K_{ij}\) shown in Table 2 indicate that the selectivity of aluminum selective electrode was improved, due to the two ring-conjugated structure and the enhanced electro negativity of center \(\text{Al}^{3+}\) in the coordination compound. Compared to other interfere ions, the electrode was only interfered by \(F^-\) relatively.

### 3.4.3. Reproducibility, response time and life time

The potential response of proposed electrode was measured 5 times in the \(\text{Al}^{3+}\) solution with concentration range of \(10^{-1}\) mol/L to \(10^{-3}\) mol/L. The table3 shown that the RSD value was in the range of 0.14% to 0.39%, which indicated the excellent reproducibility of the proposed electrode. The response time was less than 10 seconds, and the proposed electrode could be used continually three months and did not show visible loss of response characteristics.

**Table 3. Repeatability of the electrode**

<table>
<thead>
<tr>
<th>C/moL/L</th>
<th>Potential value/v</th>
<th>Average/v</th>
<th>RSD/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1.0 \times 10^{-1})</td>
<td>0.692</td>
<td>0.692</td>
<td>0.693</td>
</tr>
<tr>
<td>(1.0 \times 10^{-2})</td>
<td>0.709</td>
<td>0.709</td>
<td>0.710</td>
</tr>
<tr>
<td>(1.0 \times 10^{-3})</td>
<td>0.724</td>
<td>0.724</td>
<td>0.725</td>
</tr>
</tbody>
</table>

### 3.4. Preliminary application

To evaluate its practical applicability to real samples, the proposed aluminum ion-selective electrode was applied to the direct determination of the concentration of \(\text{Al}^{3+}\) ion in fried food sample. For the preparation of samples, 2.5g crushed sample of fried food was ashed at 650°C for 0.5h, and then dissolved with 15mL 20%(v/v) sodium hydroxide solution. After filtration, 235mL water was added into the filtrate. The solution was adjusted to pH 4, and diluted to 250mL. The potential response
value was measured 3 times, and the results were shown in Table 4. Compared to the method of Spectrophotometry, the results were satisfactory with RSD value of 4.3\% to 5.0\%.

**Table 4.** Measurement of fried paste sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measurement μg/mL</th>
<th>Standard value μg/mL</th>
<th>Average μg/mL</th>
<th>RSD %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fries</td>
<td>1.29, 1.35, 1.39</td>
<td>1.34</td>
<td>1.34</td>
<td>5.0</td>
</tr>
<tr>
<td>Chicken nuggets</td>
<td>1.70, 1.74, 1.76</td>
<td>1.72</td>
<td>1.73</td>
<td>4.3</td>
</tr>
<tr>
<td>Fritters</td>
<td>1.98, 2.04, 2.12</td>
<td>2.10</td>
<td>2.05</td>
<td>4.9</td>
</tr>
</tbody>
</table>

4. CONCLUSION.

**Table 5.** Comparison of Al(III) selective electrode based on SSDA with those previously reported in literature

<table>
<thead>
<tr>
<th>Ionophore</th>
<th>Slope mV/decade</th>
<th>pH range</th>
<th>Life time</th>
<th>Detection limit mol/L</th>
<th>Linear range mol/L</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis(5-phenylazo salicyaldehyde) 2,3-naphthalene diimine</td>
<td>19.3±0.8</td>
<td>3.5-5.0</td>
<td>&gt;2months</td>
<td>2.5×10⁻⁶</td>
<td>5.0×10⁻⁶~1.0×10⁻²</td>
<td>[26]</td>
</tr>
<tr>
<td>N,N'bis(salecyclidene)-1,2-phenylenediamine</td>
<td>19.8±0.3</td>
<td>3.2-4.5</td>
<td>6.0×10⁻⁷</td>
<td>8.0×10⁻⁷~3.0×10⁻²</td>
<td>[27]</td>
<td></td>
</tr>
<tr>
<td>2-(4,5-dihydro-1,3-imidazol-2-yl)phenol</td>
<td>19.3</td>
<td>3.0-8.0</td>
<td>3 months</td>
<td>7.0×10⁻⁷</td>
<td>1.0×10⁻⁶~1.0×10⁻¹</td>
<td>[28]</td>
</tr>
<tr>
<td>AlMCM-41</td>
<td>19.8±0.4</td>
<td>2-6</td>
<td>&gt;4 months</td>
<td>4.6×10⁻⁷</td>
<td>1.0×10⁻⁶~1.0×10⁻¹</td>
<td>[29]</td>
</tr>
<tr>
<td>1,8-dihydroxyanthraquione</td>
<td>20.7±0.5</td>
<td>2.0-5.0</td>
<td>3 months</td>
<td>5.0×10⁻⁷</td>
<td>1.0×10⁻⁶~1.0×10⁻¹</td>
<td>[30]</td>
</tr>
<tr>
<td>Glyoxal-bis-thiosemicarbazone</td>
<td>20.1</td>
<td>2.5-4.5</td>
<td>&gt;1 months</td>
<td>8.7×10⁻⁶</td>
<td>1.8×10⁻³~1.0×10⁻¹</td>
<td>[31]</td>
</tr>
<tr>
<td>bis(5-sulphonate salicyaldehyde) 2,3-diaminobenzene</td>
<td>15.6</td>
<td>3.5-4.5</td>
<td>&gt;3months</td>
<td>5.1×10⁻⁶</td>
<td>1.0×10⁻³~1.5×10⁻¹</td>
<td>This work</td>
</tr>
</tbody>
</table>

On the basis of the results discussed in this paper, bis (5-sulphonate salicyaldehyde) 2,3-diaminobenzene can be considered as ionophore for the construction of a PVC-based matrix ISE for...
The determination of Al³⁺ ion in solution. The proposed Al³⁺ selective electrode exhibits good linear response and is reasonably selective and sensitive for Al³⁺. The electrode could be used continually two months and did not show visible loss of response characteristics. The electrode was successfully applied for direct potentiometric determination of Al³⁺ content of some real fried sample. Table 5 lists linear range, detection limit, lifetime, pH range and slope of some of the Al³⁺-selective electrodes against proposed selective electrode for comparative purposes.

ACKNOWLEDGEMENT
The authors acknowledge the kind financial support provided by the National Natural Science Foundation of China (No. 21071100), the Public Welfare Scientific Research Project of Liaoning Province of China (No. 2012003003), and the Foundation of Shenyang University of Chemical Technology (No. 20063209).

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