Ion Selective Membrane Electrodes Based on Precipitated Nitron Halides & Nitron Thiocyanate

RAJESH CHANDRA MISRA & M C CHATTOPADHYAYA*
Department of Chemistry, University of Allahabad, Allahabad 211 002

Received 11 May 1987; revised 29 December 1987; accepted 14 January 1988

The preparation of new electrodes for Br\textsuperscript{−}, I\textsuperscript{−} and SCN\textsuperscript{−} ions based on precipitated nitron bromide, nitron iodide, nitron thiocyanate as electroactive materials and silicon rubber as inert binder is described. The working pH ranges for bromide, iodide and thiocyanate selective electrodes are 2-13, 2-10 and 3-8, respectively. Both the bromide and iodide selective electrodes show linear response in the concentration range of 1 x 10\textsuperscript{−1} M to 1 x 10\textsuperscript{−5} M. The thiocyanate selective electrode shows linear response in the concentration range of 1 x 10\textsuperscript{−5} M to 5 x 10\textsuperscript{−4} M. The response times of the bromide, iodide and thiocyanate selective electrodes are 10 sec, 20 sec and 15 sec, respectively. The selectivity coefficients for different anions for all the three electrodes have been evaluated. These electrodes are found to be useful in electrometric titrations.

Nitron can be precipitated by various monovalent anions\textsuperscript{1}. In this laboratory a nitrate selective electrode based on precipitated nitron nitrate was prepared\textsuperscript{2} and found suitable for direct determination of NO\textsubscript{3}\textsuperscript{−} in the presence of other anions, except I\textsuperscript{−} which caused interference. The present work was undertaken to see if precipitated nitron bromide, iodide and thiocyanate could be used for the preparation of ion selective membrane electrodes for the determination of Br\textsuperscript{−}, I\textsuperscript{−} and SCN\textsuperscript{−}, respectively and to see to what extent other halides and other anions interfere in the working of such electrodes. The characteristics of these electrodes have been examined in detail.

Preparation of master membranes

Brown coloured nitron bromide, ash coloured nitron iodide and black coloured nitron thiocyanate precipitates were obtained by adding respectively Br\textsuperscript{−}, I\textsuperscript{−} and SCN\textsuperscript{−} to a solution of nitron (0.5 g) in 20% (v/v) acetic acid. After washing and drying the precipitates, the master membrane with each precipitate was prepared\textsuperscript{2} by mixing each of the precipitates (100 mg) with silicon rubber (400 mg).

Preparation of electrodes

A small portion from each nitron halide and nitron thiocyanate membranes was cut and plugged at one end of the glass tube (outer diameter 0.8 cm, inner diameter 0.5 cm) with the help of Araldite (Ciba-Geigy). These tubes were filled with 0.1 M solution of KBr, KI and KSCN, respectively. In each of these tubes was added a 0.1 M solution of KCl. A saturated calomel electrode was inserted for electrical contact. A separate saturated calomel electrode was used as an external reference electrode. Thus the three electrode systems can be represented as follows:

SCE CI\textsuperscript{−} (0.1 M) \times (0.1 M) Membrane Sample SCE

where X is Br\textsuperscript{−}, I\textsuperscript{−}, SCN\textsuperscript{−}.

Before taking measurements each electrode system was kept immersed for six days in 0.1 M solution of respective anion.

Three separate sets of solutions of KBr, KI and KSCN were prepared in which the concentration was varied in the range of 1 x 10\textsuperscript{−1} M to 1 x 10\textsuperscript{−6} M and the potential was recorded with respective ion selective electrode with the help of Philips pH meter PR-9405M at room temperature (25° ± 2°C). The response of each electrode was plotted against the concentration of respective ion in a semilog graph paper and it was observed that in the case of bromide and iodide selective electrodes, a linear response was obtained down to 1 x 10\textsuperscript{−5} M concentration of the respective ion and for the thiocyanate selective electrode linear response was observed down to thiocyanate concentration of 5 x 10\textsuperscript{−6} M. Other properties like response time, pH range, age of the membrane of all the three electrodes were determined (Table 1). The selectivity coefficients were determined by mixed solution method\textsuperscript{1−5} (Table 2).

Though the iodide ion interfered with the bromide selective electrode, the reverse was not true. There was no interference of iodide ion on thiocyanate selective electrode. The presence of nitrate ion had very

Table 1—Characteristics of Ion Selective Membrane Electrodes

<table>
<thead>
<tr>
<th>Ion selective electrode</th>
<th>Lower detection limit (M)</th>
<th>Per decade change in potential (mV)</th>
<th>Response time (sec)</th>
<th>Working pH range</th>
<th>Life of electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromide</td>
<td>1 x 10\textsuperscript{−5}</td>
<td>60</td>
<td>10</td>
<td>2-13</td>
<td>Over 6 months</td>
</tr>
<tr>
<td>Iodide</td>
<td>1 x 10\textsuperscript{−5}</td>
<td>50</td>
<td>20</td>
<td>2-10</td>
<td>8 months</td>
</tr>
<tr>
<td>Thiocyanate</td>
<td>5 x 10\textsuperscript{−6}</td>
<td>40</td>
<td>15</td>
<td>3-8</td>
<td>Over 6 months</td>
</tr>
</tbody>
</table>
Table 2—Selectivity Coefficients of Ion Selective Membrane Electrodes at 25 ± 2°C

<table>
<thead>
<tr>
<th>Ion selective electrode</th>
<th>Selectivity coefficient in presence of interfering anion (0.001 M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F⁻</td>
</tr>
<tr>
<td>Bromide</td>
<td></td>
</tr>
<tr>
<td>Iodide</td>
<td>5.0</td>
</tr>
<tr>
<td>Thiocyanate</td>
<td>5.0</td>
</tr>
</tbody>
</table>

a selectivity coefficient value of ~0 indicates there is no interference at all concentrations.

Application

In order to explore the utility of these electrodes in potentiometric titrations, precipitation titrations of soluble silver salt against halide ion was performed using all the three selective electrodes as indicator electrodes.

For titration standard solutions of halide ion (potassium salts) and silver ion were prepared. Usually three sets of solutions for each halide ion were titrated in which concentrations were varied from 0.01 M to 0.001 M. In all cases there was a sharp increase in the value of electrode potential at the equivalence point (Fig. 1).

The authors are thankful to State Council of Science and Technology, U P, Lucknow for financial help.

References