Chapter 6

Sulphate ion selective electrode
6.1 INTRODUCTION

Electrochemical sensors have played an important role in the development of sensors for selective determination of chemical species at low concentrations [1, 2]. Ion-selective electrodes (ISEs) are one of the most exciting developments in the field of electro-analytical chemistry. The interest in ISEs have grown over recent years as they are portable, easy, and can provide accurate rapid measurements with reasonable sensitivity and selectivity [3,4]. Though there have been numerous reports of cation-selective electrodes and few anion-selective electrodes, the primary study was mainly restricted to cation ISEs and there are still investigations that use anion-selective electrodes for selectivity, detection limit, and selective determination of particular anion of interest [4-9]. Anion-selective membrane electrodes using selective ionophores to respond to anions following the Hofmeister selectivity tend to diminish response for decreasing lipophilicity [10]. Sulphate and phosphate are highly hydrophilic anions, and electrodes based on such anions function very poorly in aqueous solutions as compared to lipophilic anions in the early Hofmeister series members. It is still highly challenging to achieve useful selectivity for sulphate over hydrophobic anions by receptor-based chemical sensors such as selective electrodes. This is due to the high hydrophilicity of such anions (sulphate and phosphate), which leads to the difficulty of compensating for large differences in Gibb’s free energies of transfer between sulphate and interfering anions by selective complexation. The effect of solvating environment at the interface inherently suitable for the recognition of hydrophilic substrates and the reverse effect to bulk two-phase distribution systems and the notochord of complete dehydration of hydrophobic anions for interfacial selectively binding to hydrophilic anions over hydrophobic anions.

The sulphate ion has a significant role in biological, medical and environmental fields, such as elimination of pollution in water. Commonly, sulphate is present in water in association with calcium, iron, magnesium and sodium ions as salts and hence, the determination of sulphate by sensitive, rapid, precise, and accurate methods is important in assessing the salinity and quality of water [11, 12]. Sulphate is one of the dominant sulphur species in aquatic environments. Environmental sulphate pollution originates mainly from plants where sulphuric acid is used. Major sources of sulphate
release into water and the atmosphere are: leaching from the soil due to high solubility of magnesium, potassium, and sodium sulphate salts, decaying plant and animal matter, and numerous chemical products. The presence of sulphate in drinking water affects its aesthetic quality but does not pose an immediate threat to public health as recommended by the World Health Organization [13, 14], but increasing sulphate levels in water provide a strong indicator for acidification of water bodies due to water pollution, causing health concerns regarding water quality [15-16]. Therefore, development of accurate and reliable methods for sulphate ion determination is very important. Existing methods for sulphate determination have several drawbacks, such as: long duration and unacceptability for low concentrations (gravimetric methods); laboriousness, and insufficient selectivity and reproducibility (optical methods including nephelometry and turbidimetry) [17]; or complexity and high equipment cost (capillary electrophoresis) [18-20].

For a better ion-selective electrode, a strong interaction between the ionophore and the anion is essential in order to complex anions selectively, and the potential response is believed to be based on this characteristic of the membrane. Recent trends showed an increasing demand for developing novel ionophores [21]. A variety of approaches for designing and bringing possible combinations of membrane compositions for sulphate-ion-selective electrodes as evidenced in the literature. The first ion-selective electrode for the sulphate anion was made by Hirsch-Ayalon in 1965 [22]. Pungor and Havas in 1966 and Rechnitz et al. in 1967 prepared sulphate-selective membranes using a precipitate-impregnated silicone rubber [23, 24]. Although these electrodes exhibited a relatively good potentiometric response, their selectivity toward the sulphate ion was not sufficient [25]. In 1998, Nishizawa et al. [26] prepared the first sulphate-selective electrode based on PVC. In 1999, Li et al. [27] investigated the response mechanism of the electrode by ac impedance. Then, a zwitterionic bis(guanidinium) by Fibbioli et al. [28] a Schiff base complex of Zn(II) by Shamsipur et al. [29] and pyrillium perchlorate derivatives by Ganjali et al. [30] were used as ionophores for the preparation of a sulphate ion selective electrode. Sathyapalan et al. [31] predicted the optimal recognition site by a density functional theory simulation for the design of a sulphate-selective electrode. Recently, A new anion-selective polyvinyl chloride (PVC) membrane electrode based on {6,6′ -diethoxy-2,2′-[2,2-
dimethylpropane-1,3-diylbis-(nitromethylidyne)]-diphenolato} nickel(II) monohydrate as a carrier based on electrochemical impedance spectroscopy is reported [32].

Recently, intensive research has been directed towards preparation of a variety of selective receptors for anions. For the design of a suitable ionophore for anions, the host-guest interaction via hydrogen bonding and solvating environment are crucial factors [33]. The Schiff bases (SB) are known to form stable complexes with transition metal ions, and they act as ion carriers in the polymeric membrane. Almost all the metals form 1:1 metal complexes with SBs. The feature of SBs gives geometric and cavity control of host–guest complexation and modulation of its lipophilicity, and produce remarkable selectivity, sensitivity and stability for a specific ion. The resulting complexes have attracted increasing attention in the domain of ionic interaction due to their unique properties and reactivity.

Compared with these first two types of ionophores, the design of synthetic receptors capable of hydrogen-bond formation with anions is less well developed [34]. One of the advantages of incorporating hydrogen-bond forming functionalities, such as guanidinium, urea, and thiourea, into the overall architecture of an ionophore is that they are directional. This allows for the design of ionophores having a specific shape, which can bind anions of a particular geometry better than others [35].

In this work, we introduce a novel hydroxyl Schiff molecule in combination with plasticizer and cation excluder for the selective determination of sulphate. The principle for designing our ionophore was based on hydrogen bonding, solvating environment and dielectric property. The electrode was investigated for the study of selectivity and sensitivity for sulphate ion in the presence of the various other ions. The electrode was used for different aspects of ion selective electrode study. A sulphate sensor showed improved workable pH range, fast response time and reasonable reproducibility as compared to previously reported sulphate selective electrodes [22-32].
6.2 EXPERIMENTAL

6.2.1 Reagents

Analytical reagent grade chemicals and double distilled water were used. Dibenzoyl methane, carbohydrazide, high molecular weight poly (vinylchloride) powder (PVC), dibutyl phthalate (DBP), bis(2-ethylhexyl)sebacate (EHS), tributyl phthalate (TBP) and tetrahydrofuran (THF) were obtained from Sigma. Trioctyl methyl ammonium chloride (TOMAC) and 2-nitrophenyl octyl ether (NPOE) were obtained from Fluka. Salts of metal nitrates or chlorides and solvents like methanol, ethanol, diethylether, acetonitrile, nitric acid and hydrogen peroxide (all from Merck) were of the highest purity available and used without any further purification. All the metal nitrate solutions were freshly prepared by accurate dilution from their stock solution of 1 M, with distilled, de-ionized water. A series of test solutions (10^{-8}, 10^{-7}, 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, and 10^{-1} M) were prepared.

6.2.2 Synthesis of ionophore

The synthesis and characterisation of the ionophore bis(dibenzoylmethane carbohydrazone), BBMC is discussed in Chapter 2 and Section 2.6. The structure of the ionophore is shown as Figure 6.1.

![Figure 6.1 Structure of Bis(dibenzoylmethane carbohydrazone), BBMC](image_url)
6.2.3 Fabrication of electrode

The viscous solution that was used for the formation of the membrane was prepared by mixing powdered PVC, EHS and TOMAC in 5 cm$^3$ of THF. The resulting, low-viscosity mixture was thoroughly mixed and transferred into a glass dish of 2 cm in diameter and then, its solvent was slowly evaporated to gain an oily concentrated mixture. Consequently, the membrane was formed on the tip of a Pyrex tube (3-5mm o.d.) and by dipping the tube into the mixture for about 10 s, so that a transparent membrane of about 0.3mm thickness was formed. Before being filled with an internal filling solution, the tube was pulled out and given enough time to dry at room temperature for about 16 h.

6.2.4 Conditioning and potential measurement

All potentiometric measurements were performed at room temperature. The polymeric membrane electrode was equilibrated for ~24 hours in 1.0 × 10$^{-1}$ M Na$_2$SO$_4$ solution. The potentials were measured by varying the concentration of Na$_2$SO$_4$ in test solution in the range 1 × 10$^{-9}$ M to 1.0 × 10$^{-1}$ M. Standard Na$_2$SO$_4$ solutions were obtained by gradual dilution of 10$^{-1}$ M Na$_2$SO$_4$ solution.

The emf measurements with the polymeric membrane electrode were carried out on digital potentiometer at 25 ± 1°C using saturated calomel electrode (SCE) as reference electrode with the following cell assemblies:

\[
\text{Hg–HgCl}_2, \text{ KCl (sat) } | \text{internal solution 1.0} \times 10^{-4} \text{ M SO}_4^{2-} \text{ PVC membrane } | \text{test solution } | \text{Hg}_2\text{Cl}_2-\text{Hg, KCl (sat.)}
\]

6.3 RESULTS AND DISCUSSION

6.3.1 Preliminary investigation

In preliminary experiments, to investigate the suitability of ionophore BBMC, different membrane electrodes with this carrier were prepared and their potentiometric responses to different anions like perchlorate, salicylate, thiocyanate, iodide, nitrate, bromide, citrate, chloride, thiosulphate, sulphate, acetate, sulphite, dihydrogen phosphate, fluoride, oxalate and hydrogen carbonate were measured. As observed in
Figure 6.2, except for $\text{SO}_4^{2-}$, all other anions tested showed weak responses due to lower interaction with the ionophore in the membrane. Therefore, the membrane electrode based on BBMC was found to be highly responsive to sulphate ion relative to several other anions. Then, to test the membrane, various performance characteristics were investigated, such as the effect of membrane composition, selectivity, response time, sensitivity, life time, working range of the electrode at different activities of the anion, and pH were investigated.

6.3.2 Optimization of membrane composition

It is well known that the sensitivity and selectivity obtained for a given neutral carrier depend significantly on the membrane composition and the properties of the solvent mediator employed as well as the PVC/plasticizer ratio used. In preparation of many PVC membrane electrodes, a plasticizer/PVC ratio (m/m) of nearly 2 has resulted in very suitable performance characteristics [36]. Thus the influences of the membrane composition, nature, amount of plasticizer, and the lipophilic additives on the potential response were investigated. Several membranes were prepared with different compositions. The optimized membrane compositions are summarized in Table 6.1 and Figure 6.3.

6.3.2.1 Influence of plasticizer

As membrane solvent, plasticizers can greatly affect the response of ion-selective electrodes (ISEs). Plasticizers for use in membranes should exhibit high lipophilicity, high molecular weight, low tendency for exudation from the polymer matrix, low vapour pressure, high capacity to dissolve the substrate and other additives present in the membrane, and adequate dielectric constant [37]. Further improvement in the performance has been attempted by the addition of appropriate amounts of different plasticizers (EHS, TBP, DBP, BA and NPOE) to the membranes. Among the several membranes tested for the ionophore, membranes incorporating EHS showed better potentiometric responses, i.e., higher sensitivity and wider linearity of the calibration plots (sensor no. 4). It seems that EHS, offering adequate polarity and relatively high
mobility with respect to other plasticizers examined, provides appropriate conditions for incorporation of the less lipophilic sulphate ion.

Figure 6.2 Potential response of ligand BBMC to $A^{n+}$ ion

Figure 6.3 Optimized membrane composition
6.3.2.2 Influence of ionic additive

The effect of the incorporation of an ionic lipophilic additive to the membranes was evaluated by studying the potentiometric response of membranes containing PVC, EHS and the corresponding ionophore [S. No. 4], with and without ionic additive [S. No. 7]. The membranes without ionic additive showed a practically negligible response for all the anions assayed, while those containing the additive showed a Nernstian response portion for most anions assayed, as is shown in Figure 6.2. As it is well known that the presence of lipophilic ionic sites with a charge sign opposite to that of the primary ion are decisive for obtaining a good response of ionophore-based ISEs [38]. The influence of the additive/ionophore molar ratio in the membrane composition [Table 6.1] in the response to the different anions was also studied. As the ratio increased to 0.6, the response of the membranes containing ionophore increased for all the anions assayed, while the anti-Hofmeister behavior remained. However, when this ratio was further increased to 0.7, the anti-Hofmeister response achieved for the divalent anions decreased. According to these results, sensor no. 4 containing EHS and a 0.6 additive/ionophore molar ratio, were selected for further studies.

6.3.3 Anion-binding studies

The affinity of ionophore for various anions was determined by UV–vis spectroscopic method. Figure 6.4 (A) shows the absorption spectrum of ionophore (1.0 × 10⁻³ M) in DMSO and Figure 6.4 (B), upon addition of equal volume of sulphate ion (1.0 × 10⁻³ M) in the ionophore. It is seen that the absorption increases after the addition of sulphate ion, which showed the interaction with ionophore.
## Table 6.1 Optimization of membrane composition

<table>
<thead>
<tr>
<th>S. No.</th>
<th>PVC (wt.%)</th>
<th>Plasticizer (wt.%)</th>
<th>Ionophore (wt.%)</th>
<th>TOMAC (wt.%)</th>
<th>Slope (mV/decade)</th>
<th>Detection limit (M)</th>
<th>Linear Range (M)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>31</td>
<td>56(DBP)</td>
<td>3</td>
<td>1</td>
<td>19.5</td>
<td>$1.0 \times 10^{-5}$</td>
<td>$1.0 \times 10^{-5} - 1.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>2</td>
<td>31</td>
<td>65(TBP)</td>
<td>2</td>
<td>2</td>
<td>20.7</td>
<td>$3.8 \times 10^{-6}$</td>
<td>$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>3</td>
<td>31</td>
<td>64(BA)</td>
<td>2.5</td>
<td>2.5</td>
<td>15.4</td>
<td>$4.0 \times 10^{-6}$</td>
<td>$1.0 \times 10^{-6} - 1.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>4</td>
<td>32</td>
<td>60(EHS)</td>
<td>5</td>
<td>3</td>
<td>29.3</td>
<td>$1.8 \times 10^{-9}$</td>
<td>$1.0 \times 10^{-9} - 1.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>5</td>
<td>32</td>
<td>59.5(EHS)</td>
<td>5</td>
<td>3.5</td>
<td>32.7</td>
<td>$1.0 \times 10^{-7}$</td>
<td>$1.0 \times 10^{-7} - 1.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>6</td>
<td>32.5</td>
<td>60(EHS)</td>
<td>5</td>
<td>2.5</td>
<td>28.7</td>
<td>$1.0 \times 10^{-10}$</td>
<td>$1.0 \times 10^{-7} - 1.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>7</td>
<td>33</td>
<td>63(EHS)</td>
<td>4</td>
<td>0</td>
<td>11.9</td>
<td>$7.0 \times 10^{-7}$</td>
<td>$1.0 \times 10^{-8} - 1.0 \times 10^{-9}$</td>
</tr>
<tr>
<td>8</td>
<td>33</td>
<td>61(NPOE)</td>
<td>5</td>
<td>1</td>
<td>17.5</td>
<td>$1.7 \times 10^{-8}$</td>
<td>$1.0 \times 10^{-8} - 1.0 \times 10^{-7}$</td>
</tr>
<tr>
<td>9</td>
<td>33</td>
<td>61(NPOE)</td>
<td>4</td>
<td>2</td>
<td>23.1</td>
<td>$2.0 \times 10^{-6}$</td>
<td>$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>10</td>
<td>33</td>
<td>60(NPOE)</td>
<td>4</td>
<td>3</td>
<td>24.8</td>
<td>$1.4 \times 10^{-3}$</td>
<td>$1.0 \times 10^{-3} - 1.0 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
Figure 6.4 UV-Visible interaction mechanism of (A) BBMC (1×10^{-3} M) in DMSO and (B) BBMC with SO_4^{2-} (1×10^{-3} M) in DMSO
6.3.4 Membrane study

The polarizing optical microscope is a useful technique to study the distribution of various components in the membrane. So, the membrane is observed under optical microscope to study the incorporation of ionophore with plasticizer and additive in the PVC matrix [Figure 6.5]. The given Figure 6.5 (A) shows the long needle like structure distributed all throughout the membrane. It was before the potentiometric study of the membrane was done whereas in the Figure 6.5 (B), the membrane was viewed after the potentiometric study. It can be easily observed that the membrane after use was found to be saturated and capturing sites were blocked.

Figure 6.5 Membrane picture under polarized optical microscope (A) before potentiometric study (B) after potentiometric study

6.3.5 Internal solution effect

Usually, a relatively high concentration of primary ion solution is used in the composition of the internal filling solution [39]. However, recent findings have shown that this procedure has adversely affects the detection limit due to the flux of the primary ion from the inner solution to the sample solution [40]. This flux competes at the membrane/solution interface with the primary ion arising from the bulk of the sample. For this reason, a relatively diluted internal filling solution, $10^{-4}$ M, of
Na₂SO₄ was used. The calibrations of the different anions assayed were made in water in order to avoid the contribution of any other anion to the membrane potential [41].

6.3.6 Calibration and statistical data

The emf response of the proposed electrode based on ionophore BMBC, at varying concentrations of sulphate ion [Figure 6.4] indicated a linear range from 1.0 × 10⁻⁹ - 1.0 × 10⁻² M. The slopes of the calibration curves were 29.3 ± 0.4 mV per decade of SO₄²⁻ ion concentration. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 1.8 × 10⁻⁹ M.

6.3.7 Selectivity

Selectivity is the most important characteristic of ISEs since this parameter provides information on the ability of the sensing membrane to discriminate the primary ion from other ions of the same charge sign. In this work, the selectivity coefficients of the sensors toward different anionic species (A⁻) were evaluated by using the matched potential method (MPM) [42]. Unbuffered solutions were used in these studies to avoid any contribution from the buffer anions [43]. The values for the ISE containing the blank membrane were also obtained for comparison purposes. Following the recommendations of Bakker et al. [44] to avoid biased values, no selectivity coefficients were calculated for interfering anions which did not show a Nernstian portion in the calibration graph. It is given by expression:

$$\log K_{SO_4^{2-}A^n-}^{pot} = \log(a'_{SO_4^{2-}} - a_{SO_4^{2-}}) - \log(a_{A^n-})$$

In the present studies a_{SO_4^{2-}} and a'_{SO_4^{2-}} were kept at 1.0×10⁻⁶ M and 5.0×10⁻⁶ M and a_{A^n-} was experimentally determined. A value of selectivity co-efficient equal to 1.0 indicates equal response to both primary ion and interfering ions. The value <1.0 shows that the sensor is selective to the primary ion over the interfering ion. It is seen from Table 6.2 that the selectivity coefficients determined are sufficiently <1.0, indicating that the present sensors are significantly selective to sulphate ion over all the interfering ions. The electrode responded in the following order of preference to
anions: SO$_4^{2-}$ > ClO$_4^-$ > IO$_4^-$ > C$_6$H$_4$OHHCOO$^-$ > CrO$_4^{2-}$ > SCN$^-$ > C$_6$H$_3$O$_7^{2-}$ > CO$_3^{2-}$ > HPO$_4^{2-}$ > CH$_3$COO$^-$ > BrO$_3^-$. This anion-selectivity pattern deviated remarkably from that imposed by the hydrophobicity-based Hofmeister sequence (ClO$_4^-$ > SCN$^-$ > I$^-$ > C$_6$H$_4$OHCOO$^-$ > NO$_3^-$ > Br$^-$ > Cl$^-$ > HCO$_3^-$ > CH$_3$COO$^-$ > SO$_4^{2-}$ > HPO$_4^{2-}$). As can be seen, excellent selectivity coefficients on the order of 10$^{-2}$ and lower are obtained for a large number of inorganic and organic anions, indicating insignificant interfering effect of these anions on sulphate ion determination by the proposed membrane sensor.

**Table 6.2 Potentiometric selectivity coefficient ($K_{SO_4^{2-},A^n-}^{pot}$) for interfering ions**

<table>
<thead>
<tr>
<th>Interfering ion</th>
<th>$K_{SO_4^{2-},A^n-}^{pot}$</th>
<th>Interfering ion</th>
<th>$K_{SO_4^{2-},A^n-}^{pot}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_6$H$_4$OHHCOO$^-$</td>
<td>5.28 × 10$^{-3}$</td>
<td>PO$_4^{3-}$</td>
<td>7.12 × 10$^{-2}$</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>7.1 × 10$^{-3}$</td>
<td>C$_6$H$_3$O$_7^{2-}$</td>
<td>2.95 × 10$^{-3}$</td>
</tr>
<tr>
<td>SCN$^-$</td>
<td>3.83 × 10$^{-3}$</td>
<td>CrO$_4^{2-}$</td>
<td>5.01 × 10$^{-3}$</td>
</tr>
<tr>
<td>IO$_4^-$</td>
<td>6.1 × 10$^{-3}$</td>
<td>NO$_3^-$</td>
<td>2.20 × 10$^{-3}$</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>2.5 × 10$^{-3}$</td>
<td>SO$_3^{2-}$</td>
<td>1.7 × 10$^{-3}$</td>
</tr>
<tr>
<td>CH$_3$COO$^-$</td>
<td>1.54 × 10$^{-2}$</td>
<td>Cl$^-$</td>
<td>7.96 × 10$^{-2}$</td>
</tr>
<tr>
<td>BrO$_3^-$</td>
<td>1.39 × 10$^{-2}$</td>
<td>HPO$_4^-$</td>
<td>2.47 × 10$^{-2}$</td>
</tr>
</tbody>
</table>

**6.3.8 pH Effect**

The working pH range of the electrode was assessed by taking a series of solutions of sulphate with 10$^{-4}$ M concentration, adjusting the pH from 2 to 10 (by H$_3$PO$_4$ or NaOH). The potential of each solution was measured and plotted against the respective pH value [Figure 6.6]. The deviation in electrode potential at pH above 8.0 may be due to interference of hydroxide ion. Below pH 3.0, sulphate is partially converted into hydrosulphate predominating in the SO$_4^{2-}$/HSO$_4^-$ equilibrium and also decreased the hydrogen bonding between sulphate ion and hydrogen of ionophore. Hence, the working pH range of electrode is 3.0–8.0.
6.3.9 Effect of non-aqueous media

As the samples may possess some non-aqueous content in them, hence the performance of the proposed electrode is also assessed in non-aqueous media using methanol-water, ethanol-water, acetone-water and acetonitrile-water mixtures. The non-aqueous content was varied between 10 and 35% (v/v). The sensor does not show appreciable change in detection limit ($2.8 \times 10^{-9}$ M) or slope ($29.1 \pm 1.0$ mV decade$^{-1}$ activity) in mixture up to 30% (v/v) non-aqueous content except for acetone-water mixture [Figure 6.7, Table 6.3]. However, in mixtures having higher percentage of non-aqueous content (>30%), the detection limit and the slope both deteriorate from the usual slope. Such an observed behaviour can be explained on the basis of leaching of the ionophore in organic phase.

6.3.10 Response time and life time study

The response time of an ISE is an important parameter that must be considered if the sensor is going to have any type of practical utility. The resulting data depicted in...
**Figure 6.7 Comparison of slopes of Sulphate ISE in non aqueous media**

**Figure 6.8** shows that the time required to achieve a steady potential after successive immersion of a series of sulphate ions, each having a tenfold difference in activity, is ~12 s. On the other hand, in order to evaluate the reversibility of the proposed electrodes, a similar procedure in the opposite direction was adopted. The measurements were performed in the sequence of high to low from $1.0 \times 10^{-2}$ to $1.0 \times 10^{-9}$ M sample activities. The results showed that the potentiometric responses of the electrode were reversible, although the time required reaching equilibrium values (70 s) was longer than that for the low-to-high sample activities.

The lifetime of an ion-selective electrode is usually defined as the time interval between the conditioning of the membrane and the moment when at least one of its response characteristics changes. One of the criteria to assess the lifetime is the extent of leaching of the ionophore from the membrane. This in turn depends on the properties of the plasticizer and the additive being used, and their compatibility with the ionophore [45]. It was observed that there was no significant change in the slope of the curve on successive days. The S. No. 4 was tested over a period of 3 months to investigate its stability. The sulphate-selective electrode worked over a period of at
Table 6.3 Electrode response in mixed solvent media

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Percentage (%) (v/v)</th>
<th>Slope (mV/decade)</th>
<th>Detection limit (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>20</td>
<td>29.1</td>
<td>2.8 × 10⁻⁹</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>28.9</td>
<td>2.4 × 10⁻⁸</td>
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<tr>
<td></td>
<td>35</td>
<td>32.4</td>
<td>1.4 × 10⁻⁶</td>
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<tr>
<td>Ethanol</td>
<td>20</td>
<td>29.2</td>
<td>3.0 × 10⁻⁹</td>
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<td></td>
<td>30</td>
<td>29</td>
<td>2.6 × 10⁻⁸</td>
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<tr>
<td></td>
<td>35</td>
<td>33.7</td>
<td>3.9 × 10⁻⁵</td>
</tr>
<tr>
<td>Acetone</td>
<td>20</td>
<td>28.9</td>
<td>1.2 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>26</td>
<td>4.5 × 10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>18.1</td>
<td>3.4 × 10⁻⁵</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>20</td>
<td>29.1</td>
<td>2.3 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>28.7</td>
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<tr>
<td></td>
<td>35</td>
<td>34.1</td>
<td>4.9 × 10⁻⁴</td>
</tr>
</tbody>
</table>

least 80 days, and no appreciable change in the calibration characteristics or response time was observed. After 80 days, changes were observed in the slope (from 29.1 to 28.4 mV decade⁻¹ of activity) and detection limit. During this period, the sensor was used for 2 h a day and 3 days a week. During no usage, the electrode was stored under dry conditions in an opaque closed vessel and before use was re-equilibrated by dipping into 0.01 M $SO_4^{2-}$ solutions for 2 h.
6.4 ANALYTICAL APPLICATIONS

6.4.1 Potentiometric titration

The proposed membrane electrodes were found to work well under laboratory conditions. The sulphate-selective electrode was used as an indicator electrode in the successful titration of a SO$_4^{2-}$ solution (20.0 cm$^3$, $1.0 \times 10^{-6}$ M) with a Ba$^{2+}$ solution ($1.0 \times 10^{-4}$ M). The resulting titration curve is shown in Figure 6.9. It has been observed that the amount of sulphate ion can be determined accurately with the electrode. This titration was repeated three times, with an end point volume of 4.98 ±0.03 cm$^3$ of EDTA solution.
6.4.2 Real sample analysis

An attempt was made to determine sulphate ions in water samples and a drug. The different samples, collected from Yamuna River, tap water from Dwarka and New Delhi and rain water were analyzed without any treatment. The comparison of the results obtained from five measurements by sulphate ion selective electrode and atomic absorption spectrometry as shown in Table 6.4. The certified value shows good agreement between the AAS and potentiometric procedures.

The electrode was also used for the determination of zinc in a zinc sulphate tablet, orazinc 110 (from Mericon Industries,). Each tablet was dissolved in water in a 50 ml volumetric flask, 0.5 cm$^3$ of 3 M nitric acid was added and diluted to the mark with water. The resulting solution was titrated with a 1:0×10$^{-1}$ M standard BaCl$_2$ solution, using the proposed sensor as an indicator electrode. The iron content of the drug calculated from three replicate measurements (24.4 ±0.4 mg per tablet) was found to be in satisfactory agreement with the declared amount of 25 mg per tablet Table 6.4.
Table 6.4 Determination of Sulphate ion in real samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>SO$_4^{2-}$/added(ppm)</th>
<th>ISE study$^a$</th>
<th>AAS study$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yamuna water</td>
<td>-</td>
<td>4.1 ± 0.3</td>
<td>3.9 ± 0.2</td>
</tr>
<tr>
<td>Tap water</td>
<td>14.0</td>
<td>15.3 ± 0.1</td>
<td>14.5 ± 0.2</td>
</tr>
<tr>
<td>Rain water</td>
<td>14.0</td>
<td>17.9 ± 0.3</td>
<td>18.1 ± 0.2</td>
</tr>
<tr>
<td>Orizinc(drug)</td>
<td>-</td>
<td>24.4 ± 0.4</td>
<td>24.8 ± 0.2</td>
</tr>
</tbody>
</table>

6.5 CONCLUSION

It has been demonstrated that sulphate-selective electrodes plasticized by low polarity plasticizer (bis(2-ethylhexyl) sebacate) and containing bis(dibenzoylmethane carbohydrazone) BBMC as a neutral carrier and a higher quaternary ammonium salt with improved steric accessibility of the exchange center (tributylmethyl ammonium chloride) as an anion exchanger, possess rather good sulphate selectivity, low LDL value, good potential reproducibility, long lifetime and can be successfully used for sulphate determination in laboratory for titration, river, rain and sweet water, as well as in drugs. It has been shown that presence of foreign ions in the sample solution can lead both to overestimation (due to foreign anions interference) and to underestimation (due to sulphate complexation by metal cations) of sulphate content. Both undesirable effects are eliminated by sample dilution that can be also used as a simple test for correctness of results obtained. Relative error of sulphate determination by direct potentiometry method in the samples studied, did not exceed 7%. This fact, in combination with simplicity and expressness of the method, allows us to recommend it for practical use.
REFERENCES

Sulphate ion selective electrode