Hydrogen ion selective poly (vinyl chloride) membrane electrode based on 2,2'-N,N'-bis(salicyldlimino)azobenzene

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Abstract

A hydrogen ion-selective electrode poly (vinyl chloride) (PVC) membrane electrode was developed using 2,2'-N,N'-bis(salicyldlimino)azobenzene as neutral carrier. The sensor exhibits a Nernstian response for hydrogen ions over a wide concentration range (1.0×10⁻¹² to 1.0×10⁻² mol L⁻¹) with a good slope of 58.5 (± 0.6) mV / pH at 20 ºC, and detection limit (5.05×10⁻¹³ mol L⁻¹). The proposed sensor was applied for at least 2 months without any measurable divergence in potential. In addition, the proposed sensor revealed a fairly good discriminating ability towards hydrogen ions in comparison with some monovalent cations and anions. The electrode was also utilized as indicator electrode in the potentiometric titration of acids with NaOH solution.

Keywords: Hydrogen ion selective electrode; 2,2'-N,N'-bis(salicyldlimino)azobenzene; Schiff Base; potentiometry.

1. Introduction

Despite the exceptional analytical performance of the H⁺-selective glass electrode, considerable work has been devoted to the development of solvent polymeric membranes with similar properties [1–3]. Hydrogen ion polymeric membranes based on neutral carriers have already exhibited a number of advantages over the traditional glass pH electrodes, including low electric resistance, safe handling, easy preparation, and promising applications in some aggressive media. Therefore, although H⁺-ISE based on neutral carriers are characterized by much lower selectivity and narrower response ranges than glass electrodes, their application in biological [4], medical [5] and environmental [6] studies where they have most advantages over glass H⁺-ISE, are still increasing. Various ionophores for PVC membrane pH-electrode have been reported such as long-chain alkyl picolamides [7-8], amines [3, 9-13], octadecylisonicotianate [14], alkylpyrazoles [4], hexabutyl-tri-amido phosphate [15], azobenzenes[16], phenoxazine derivatives [17-19], 4',5'-dibromo fluorescin octadecyl ester [20], aliphatic, heteroaromatic and their derivatives [2, 6, 14, 21]. In most of the these designs, sensing parts of pH sensors contain weak acidic or basic groups whose dissociated and undissociated forms have different optically or electrically properties in the pH range of interest. The aim of this work is to assess the performances of a synthesized azo-Schiff base ligand in plasticized PVC matrices as a
This class of ligands is widely used as proton receptor due to basic centers as well as high intramolecular hydrogen bonding capacity [22]. 2,2′-N,N'-bis(salicylaldimino)azobenzene (Fig. 1) as an ionophore, exhibited a high sensitivity to pH in a wide range. In comparison with other pH sensors that recently have been reported [23-29], the proposed sensor has wide dynamic range and suitable Nernstian slope.

![Fig. 1. Structure of 2,2'-N,N'-bis(salicylaldimino)azobenzene.](Image)

2. Experimental

2.1. Reagent

Analytical reagents grade chemicals and doubly distilled water were used for preparing all aqueous solutions. High molecular weight polyvinyl chloride powder (PVC), dioctyl phthalate (DOP), dibutyl phthalate (DBP), tris(2-ethylhexyl) phosphate (TEHP), and tetrahydrofuran (THF) were obtained from Aldrich. Sodium tetr phenylborate (NaTPB) was obtained from Fluka. Salts of metal nitrates (all from Merck) were of the highest purity available and used without any further purification. The ligand was synthesized and purified as described elsewhere.

2.2. Preparation of 2,2′-bis(salicylaldimino)azobenzene (BSAAB)

This ligand was prepared in two steps. In the first step, into a 250 mL three-necked flask, equipped with a stirrer, low temperature thermometer, a dropping funnel and a nitrogen gas inlet and maintained under a nitrogen atmosphere, was added a solution of o-phenylenediamine (10.8 g, 100 m mol) in dry toluene (50 mL). The flask was cooled to 5 °C (ice-salt bath) and then BaO2 (20 g, 120 mmol) was added in small portion via dropping funnel. The reaction mixture was stirred for 1 h and was allowed to warm up slowly. Stirring was continued for additional 6 h. Unreacted excess of BaO2 was removed on addition of distilled water with caution.

The organic phase was extracted with toluene (3×5 mL). The organic phases were combined and concentrated by rotary evaporator and then was purified by flash chromatography. The red crystals were collected and characterized as the 2,2′-diaminoazobenzene. Mp 135 °C, yield 9.22 g (87 %). In the second step, a solution of 2,2′-diaminoazobenzene (8.5 g, 40 mmol) in ethanol (100 mL) was added drop wise to excess amount of salicylaldehyde (5.0 mL, 47.9 mmol). The reaction mixture was refluxed for 12 h. The progress of the reaction was monitored by thin layer chromatography (2:1 n-heptane:ethylacetate). The reaction mixture was cooled and a yellowish-orange solid was settled from the red solution. The solid was separated using a sinter glass funnel and washed with cold ethanol (5×5 mL) to separate un-reacted salicylaldehyde and dried in vacuo (7.6 g). The ethanol solutions were added to red mother liquor and the solution was dried using rotary evaporator.
A second crop of the product was produced which was recrystallized from hot ethanol solution (over-all, 12.6 4 g 75 %). Mp 221-223 ºC. In addition to melting point, thin layer chromatography (2:1 neptane: ethylacetate), \(^1^H\) NMR and FT-IR spectroscopies were utilized to confirm the disappearance of spectroscopic signals of starting ligand (\(\nu(N-H)\) and \(\nu(C=O)\) in FTIR; aminic and aldehydic protons in NMR) and appearance of new bands (\(\nu(C=N)\) in FTIR; iminic proton in NMR). \(^1^H\) NMR (CDCl\(_3\)): \(\delta\) 13.20 (s, OH, 2); 8.49 (s, HC=N, 2); 6.83- 7.47 (m, aromatic protons, 16). FTIR (KBr, cm\(^{-1}\))): 1610 (C=N); 2105 (N=N); 3315 (OH). Anal. calc. for C\(_{26}\)H\(_{20}\)N\(_4\)O\(_2\): C, 74.27; H, 4.79; N, 6.66, Found: C, 74.76; H, 5.02, N; 6.23.

2.3. Electrode preparation

The procedure to preparation the PVC membrane was to mix 29 mg of powdered PVC, 68 mg of plasticizer (TEHP), 2.5 mg of NaTPB and 0.5 mg of ionophore in 2.5 mL of THF. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly at room temperature until an oily concentrate mixture was obtained. A Teflon tube (5.0 mm o.d.) was dipped into the mixture for about 10 s so that a transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 6 h. The tube was then filled with internal filling solution (1×10\(^{-2}\) mol L\(^{-1}\) HCl). The electrode was finally conditioned for 24 h by soaking in a 1×10\(^{-2}\) mol L\(^{-1}\) HCl solution. An Ag/AgCl electrode was used as an internal reference.

2.4. EMF measurements

All emf measurements were carried out with the following cell assembly:

Ag/AgCl \| KCl (3 mol L\(^{-1}\)) \| internal solution 1 × 10\(^{-2}\) mol L\(^{-1}\) HCl \| PVC membrane \| test solution \| Hg\(_2\)Cl\(_2\)-Hg, KCl (satd.).

A HANA ion analyzer 302 pH / mV meter was used for potential measurements at 25.0 ± 0.1 ºC. Activities were calculated according to the Debye–Hückel procedure [30].

3. Results and discussion

3.1. Effect of membrane composition

It is well known that some important features of the PVC based membranes, such as the nature and amount of the ionophore, the properties of the plasticizer, the plasticizer / PVC ratio and particularly, the nature of the additives used, significantly influence the sensitivity and selectivity of the ion-selective electrodes [31–36]. In this study, a plasticizer / PVC ratio of about 2.3 was found to be the most suitable. It is reported that the selectivity and working concentration range of membrane sensors are affected by the nature and amount of the plasticizer used. This is due to the influence of the plasticizer on the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands [37].

As is seen from Table 1 and Fig. 2, among the three different plasticizers used, TEHP resulted in the best sensitivity. Moreover, 0.5% of BSAAB was chosen as the optimum amount of the ionophore in the PVC-membrane (no. 6). Although, neutral-carrier-based ISE membranes may work properly even when they contain only a very small amount of ionic sites (e.g., as impurities), the addition of a salt of a lipophilic ion is advisable and beneficial. In fact, it has been demonstrated that the presence of lipophilic negatively charged additives improves the potentiometric behavior of certain cation-selective electrodes by reducing the ohmic resistance and improving the response behavior and selectivity [38–41] and, in some cases, by catalyzing the exchange kinetics at the sample–membrane interface [42]. From the data presented in Table 1, it is seen that the addition of NaTPB increased the sensitivity of the electrode response.
considerably. Use of 2.5% (w/w) NaTPB resulted in a Nernstian behavior of the electrode (no. 6).

Table 1
Optimization of the membrane ingredients

<table>
<thead>
<tr>
<th>Membrane number</th>
<th>Composition (%)</th>
<th>Slope (mV/decade)</th>
<th>Linear range (mol L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>33.0 PVC 65 (DBP) 1 1</td>
<td>17 (± 0.2)</td>
<td>3.4 × 10⁻⁷-5.2 × 10⁻¹</td>
</tr>
<tr>
<td>2</td>
<td>33.0 PVC 65 (DOP) 1 1</td>
<td>22 (± 0.4)</td>
<td>4.5 × 10⁻⁸-3.2 × 10⁻³</td>
</tr>
<tr>
<td>3</td>
<td>33.0 PVC 65 (TOP) 1 1</td>
<td>42 (± 0.2)</td>
<td>2.5 × 10⁻⁸-7.1 × 10⁻²</td>
</tr>
<tr>
<td>4</td>
<td>32.0 PVC 66 (TOP) 1 1</td>
<td>48 (± 0.6)</td>
<td>1.5 × 10⁻⁸-5.8 × 10⁻¹</td>
</tr>
<tr>
<td>5</td>
<td>31.0 PVC 66 (TOP) 1 2</td>
<td>54 (± 0.5)</td>
<td>2.3 × 10⁻¹¹-8.6 × 10⁻²</td>
</tr>
<tr>
<td>6</td>
<td>29.0 PVC 68 (TOP) 0.5 2.5</td>
<td>58.5 (± 0.1)</td>
<td>1.0 × 10⁻¹²-1.0 × 10⁻²</td>
</tr>
<tr>
<td>7</td>
<td>33.0 PVC 66 (TOP) 0 1</td>
<td>38 (± 0.3)</td>
<td>3.2 × 10⁻⁹-4.6 × 10⁻¹</td>
</tr>
<tr>
<td>8</td>
<td>33.0 PVC 66 (TOP) 1 0</td>
<td>30 (± 0.4)</td>
<td>5.5 × 10⁻⁸-3.1 × 10⁻³</td>
</tr>
</tbody>
</table>

The obtained results also indicate that the best sensitivity and linear range is obtained for membrane number 6 with a PVC: TEHP: BSAAB: NaTPB percent ratio of 29:68:0.5:2.5 which resulted in a Nernstian behavior of the membrane electrode over a wide concentration range. The performance of the electrode was checked using different concentrations of HCl (1.0×10⁻⁵ - 1.0×10⁻² mol L⁻¹) and a citrate buffer with a pH of 5.6 as an internal filling solution. The slope of the electrode was the same for all filling solution. Therefore, all of the studies were carried out using 10⁻² mol L⁻¹ HCl as internal filling solution.

Fig. 2. Potential response of pH-ISEs with different plasticizers: (a) TEHP, (b) DOP, (c) DBP.

3.2. Calibration curve and statistical data

Using a series of buffer solutions in the range of pH 1–13 as analytes, the potential of the cell was measured. The potentials measured were plotted against the pH values to obtain the calibration curves. Fig. 3 shows the calibration curve of the electrode. The working range and the slope of the hydrogen–selective electrodes were obtained from the linear part of its calibration curve. The slope and the linear working range of the electrode prepared with 0.5 % BSAAB, 68
% TEHP 2.5% NaTPB and 29% PVC were found to be $58.5 \pm 0.6 \text{ mV pH}^{-1}$ that was very close to the Nernstian slope value.

![Fig. 3. Calibration curve of hydrogen ion –selective membrane electrode based on 2,2'-N,N'-bis(salicylaldimino)azobenzene (electrode no. 6).](image)

The electrode was found to have a wider linear dynamic range (pH of 2–12) than most of other recently reported electrodes [23-28]. The distorting effect in the region with pH values lower than 2 may be due to presence of anions which was added to the medium in order to adjust the ionic strength. On the other hand, the deviation in the region with pH value higher than 12 may stem from sodium cation present in the solution. To evaluate the reproducibility of this electrode, a series of membranes (10) with similar composition (no. 6) prepared and the response of these electrodes to hydrogen ion concentration was tested. The results show that the average slopes and linear dynamic ranges were $58.5 \pm 0.6 \text{ mV pH}^{-1}$ and $1.0 \pm 0.3 \times 10^{-2}$ to $1.0 \pm 0.4 \times 10^{-12} \text{ mol L}^{-1}$, respectively. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was $5.0 \pm 0.4 \times 10^{-13} \text{ mol L}^{-1}$. The standard deviation of eight replicate measurements is $\pm 0.6 \text{ mV}$.

3.3. Response Time

The average time required for hydrogen ion selective electrode no. 6 to reach a potential within $\pm 0.5 \text{ mV}$ of the final equilibrium value after successive immersion in a series of hydrogen ion solutions, each having a 10-fold difference in concentration from $1.0 \times 10^{-12}$ to $1.0 \times 10^{-2} \text{ mol L}^{-1}$ was contemplated. The results are given in Fig. 4. As can be seen, in the whole concentration range, the static response times of the membrane electrode were obtained in a very short times (about 15 s) and potentials stayed constant for at least 10 min when the potentials recorded from low to high concentrations and vice versa. This means that the response time of electrode is rapid and reversible. This is most probably due to the fast exchange kinetics of protonation and deprotonation of ionophore at the test solution-membrane interface. The membrane electrode prepared could be used for at least 45 days without observing any considerable change in response characteristics (weekly tested). Also, longer conditioning times produced no further improvement in the response. So, the optimum conditioning solution was determined to have a concentration of about $1.0 \times 10^{-3} \text{ mol L}^{-1}$ for 24 h.
Fig. 4. Dynamic response time of the membrane electrode for step changes in concentration (from low to high and vice versa); A: $1.0 \times 10^{-12}$, B: $1.0 \times 10^{-11}$, C: $1.0 \times 10^{-10}$, D: $1.0 \times 10^{-9}$, E: $1.0 \times 10^{-8}$, F: $1.0 \times 10^{-7}$, G: $1.0 \times 10^{-6}$, H: $1.0 \times 10^{-5}$, I: $1.0 \times 10^{-4}$, J: $1.0 \times 10^{-3}$, K: $1.0 \times 10^{-2}$.

3.4. Selectivity

It is reported in literature that the working range of pH electrodes was adversely affected by the anions and the cations. It is known that the presence of cations and anions reduce the lower and upper limit of detection of the electrode. Thus, these ionic impurities are expected to reduce the dynamic range of the electrode [26-28]. Therefore, the sensitivity of the electrode toward the cations such as lithium, sodium, potassium and ammonium were tested and its selectivity coefficients were evaluated by the fixed interference method (Fig. 5).

Table 2
Selectivity coefficients of various alkali metals and metal ions

<table>
<thead>
<tr>
<th>Interfering ions</th>
<th>$-\log K_{H,M}^{Pot}$</th>
<th>Interfering ions</th>
<th>$-\log K_{H,M}^{Pot}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>7.85</td>
<td>Cu$^{2+}$</td>
<td>9.35</td>
</tr>
<tr>
<td>K$^+$</td>
<td>7.94</td>
<td>Cr$^{3+}$</td>
<td>10.55</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>7.76</td>
<td>Ni$^{2+}$</td>
<td>9.41</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>7.53</td>
<td>Cd$^{2+}$</td>
<td>9.13</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>10.26</td>
<td>Mn$^{2+}$</td>
<td>9.72</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>7.24</td>
<td>Mg$^{2+}$</td>
<td>9.85</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>9.04</td>
<td>Ca$^{2+}$</td>
<td>9.62</td>
</tr>
</tbody>
</table>

Due to complex formation ability of the ionophore the effect of the other cations as interfere were tested and their selectivity coefficients were calculated and listed in Table 2.
Fig. 5. Effect of the nature of background electrolyte on the electrode response: a) H⁺, b) 0.1 mol L⁻¹ NH₄⁺, c) 0.1 mol L⁻¹ Li⁺, d) 0.1 mol L⁻¹ Na⁺, e) 0.1 mol L⁻¹ K⁺.

These results indicated that the common ions of alkali metals would not cause any significant interference, unless they are present in very high concentration. The effect of the concentration of the anions such as sulfate, bromide, iodide, thiocyanate and perchlorate on the working range of the electrode was also investigated. The working range of the proposed electrode decreased with increasing the concentration of the ligand (Fig. 6 as an example). The potentials were plotted against the pH values to obtain the calibration curves (Fig. 6). As it is seen the following sequence of anion interference was observed: ClO₄⁻ > SCN⁻ > I⁻ > Br⁻ > SO₄²⁻. In the region of low pH, where acid is extracted from the sample solution, the ligand is transformed into the cationic form. In this case, the potential is independent of the pH and is a function of the concentration of anions in the solution [43].

Fig. 6. Effect of the nature of background electrolyte on the electrode response: a) H⁺, b) 0.1 mol L⁻¹ SO₄²⁻, c) 0.1 mol L⁻¹ Br⁻, d) 0.1 mol L⁻¹ I⁻, e) 0.1 mol L⁻¹ SCN⁻, f) 0.1 mol L⁻¹ ClO₄⁻.
3.5. The analytical applications of the electrode

In order to assess the practical utility of the proposed hydrogen sensor, it was used as an indicator electrode in titration of different acids such as of hydrochloric, acetic and hydrofluoric acids. The same samples were subjected to a procedure using glass electrode. Fig. 7 and Table 3 compare the results of the titration of 25 ml of $1.0 \times 10^{-2}$ mol L$^{-1}$ HCl with 0.1 mol L$^{-1}$ of sodium hydroxide as an example with both electrodes. The results obtained by both electrodes were statistically compared and there was no significant difference between functioning of them regarding accuracy and precision as revealed by the $t$-test and $F$-test, respectively.

![Graph showing titration results](image)

**Fig. 7.** Titration of 0.1 mol L$^{-1}$ HCl with 0.1 mol L$^{-1}$ NaOH by the use of the proposed hydrogen ion-selective electrode (electrode no.6) as a potentiometric indicator electrode.

<table>
<thead>
<tr>
<th>Table 3</th>
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</table>
Titrination of 25 ml 0.01 mol L$^{-1}$ of HCl with 0.1 mol L$^{-1}$ NaOH

<table>
<thead>
<tr>
<th></th>
<th>ISE</th>
<th>Glass electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean ± SD</td>
<td>2.4850 ± 0.0167</td>
<td>2.4975 ± 0.0157</td>
</tr>
<tr>
<td>R.S.D. (%)</td>
<td>0.67</td>
<td>0.63</td>
</tr>
<tr>
<td>$t$-Test *</td>
<td>2.12</td>
<td></td>
</tr>
<tr>
<td>$F$-Test *</td>
<td>1.13</td>
<td></td>
</tr>
</tbody>
</table>

*Theoretical values of $t$ and $F$ at $P = 0.05$ are 2.36 and 3.78, respectively

4. Conclusion

PVC hydrogen ion sensor based on 2,2'-N,N'-bis(salicylaldimino)azobenzene is an efficient pH electrode, exhibiting a slope of 58.5 mV pH$^{-1}$ for the potential-pH data in the 2-12 pH range. This electrode can be a good alternative for glass electrode and it can reliably be employed as an indicator electrode in acid–base titrations especially fluoride-containing solutions. In comparison with other hydrogen electrodes that have been recently published [22-28], it has a wider working range [23-27] with better Nernstian slope [22-28]. Finally, it is possible to prepare a PVC micro electrode with the optimum composition determined in this study.
Acknowledgements

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References