

Performance Optimization and Application of A Solid-state pH Sensor Fabricated from Photocurable Non-plasticized Acrylic Film

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Abstract : Potentiometric solid-state pH sensors were fabricated from photocurable *n*-butyl acrylate matrix where the sensor film was prepared by using a simple photocuring technique. The response of the pH sensor was optimized for the photocured poly(*n*-butyl acrylate), poly(*n*BA) film by investigating the effect of different compositions of the membrane additive (a lipophilic salt, sodium tetrakis[3,5-bis(trifluoro-methyl)phenyl]borate, NaTFPB) and a hydrogen ionophore. The optimum response of the sensor was achieved when 12 mol% of NaTFPB relative to ionophore was used in the sensor film with 0.01M Tris-HCl as the pH buffer. The sensor gave a near Nernstian response (56.5 ± 1.0 mV/decade) throughout the pH range of 4-10 with good reproducibility (RSD=1.8 %, $n=15$) and selectivity against other common cations such as potassium, sodium, lithium, calcium and magnesium. The solid-state pH sensor was then applied to measure the pH of samples of different matrices such as seawater, sewage, urine, milk and cheddar cheese.

Keywords: pH sensor, photocurable acrylic film, food analysis, environmental analysis.

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Introduction

Glass electrodes are widely used in pH measurements base on potentiometric principle. Although this type of electrode shows good response to pH, it has some setbacks such as its fragility that make it unsuitable for application in *in vivo* monitoring, especially in biomedical measurements. In recent years, polymeric membrane based solid-state pH sensor has been developed as an alternative to glass electrode [1].

Among the polymers used for these membranes, plasticized poly(vinyl) chloride (PVC) was the earliest polymer matrices that had been applied. One of the important characteristic of a polymer for the construction of a solid-state ion sensor is good adhesion to the surface of the sensor transducer. Unfortunately, plasticized PVC membrane demonstrated poor adhesion on flat surface [1-6]. Thus, other alternatives such as silicone rubber (SR) and plasticized polyurethane (PU) had been employed [3, 6]. In these polymer matrices, plasticizer was known to play an important role in controlling the response because it could affect the polarity and the solvation properties of the membrane, which could also influence the selectivity of the ion-selective electrodes [2]. Even though plasticizer is important but the problem of plasticizer leaching frequently confronted plasticizer based polymer membrane. Leaching of plasticizer not only affects the sensor response but also reduces the

biocompatibility of the sensor device and hence less suitable for biomedical application. Thus, self-plasticized polymer matrices that do not need plasticizer had been introduced recently [2, 4, 6, 7].

Non-plasticized polymer matrices, e.g. methacrylic-acrylic matrices, because of their photocurability, are more compatible with microfabrication of solid-state ion sensors and also demonstrated equally good analytical performance such as durability and selectivity [4, 8-10]. Copolymers based on methacrylic-acrylic matrices have been proven successful matrices for solid-state ion sensors [2, 4, 7, 9-13]. These polymer matrices are also useful in chemical attachment of the electroactive component to the polymer membrane via reaction with the double bonds of the monomers [2, 6, 12- 14]. Hydrophobic characteristic of the sensor membrane material is also important for optimum performance of an ion-selective electrode [15, 16] and the acrylic type of matrices, which is hydrophobic [8, 17] are an advantage for non-plasticized ion sensor membrane. The ability to prepare the methacrylic-acrylic types of copolymer membranes via photocuring process provides a simple and rapid mean of sensor membrane fabrication [1, 11, 12, 17, 18].

Although photocurable acrylic membranes have been reported before for use in potassium, sodium and ammonium sensors [11, 12], there has never been any detailed investigation into the effect

of membrane components on the response of pH sensor employing this type of polymers or the application of these sensor to the determination of pH of various sample matrices. Therefore in this work, *n*-butyl acrylate (*n*BA) was chosen as a monomer to prepare a slightly cross-linked poly(*n*-butyl acrylate), poly(*n*BA) film to be used as a solid-state pH sensor. This polymer film is non-plasticized, hydrophobic, possessed good adhesion and it can be prepared via photocuring. The objective is to design a solid-state pH sensor using poly(*n*BA) based film and investigate the effect of various membrane components such as ionophore and lipophilic salt on the sensor response. The performance of the pH sensor was then evaluated through its sensitivity, selectivity and applications to some real samples analysis with varying sample matrices such as seawater, sewage, urine, milk and cheddar cheese.

Experimental

Materials

Materials for the preparation of ion-selective membranes such as *n*-butyl acrylate, 2,2-dimethoxy-2-phenylacetophenone and 1,6-hexanedioldiacrylate were purchased from Aldrich. 2-Hydroxyethyl methacrylate was from Sigma. Hydrogen ionophore I (tridodecylamine), sodium tetrakis [3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) and chlorides of potassium, sodium, lithium, calcium and magnesium were from Fluka. Tris (hydroxymethyl)aminomethane HCl (Tris-HCl) was from Duchefa Biochemie. All the chemicals were analytical grade. Standard solutions were prepared in deionised water.

Sensor fabrication

The monomer of 2-Hydroxyethyl methacrylate (HEMA) was mixed with 1.6wt% of photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPP) and drop-coated on the tip of a Ag/AgCl electrode (diameter 2mm) and then photocured under UV radiation in a UV exposure unit (RS Ltd) under constant flow of nitrogen gas for 2 min. A polymer (pHEMA) film with the thickness of ~ 0.25mm was formed. This film was then hydrated with 0.01M Tris-HCl buffer, pH7 for 5 min. The purpose of fabricating this pHEMA film is to provide an internal layer to the ion sensor replacing the internal solution of conventional ion-selective electrode. This pHEMA layer or the 'internal solution' will provide a well-defined mechanism of charge transfer between the ion-selective membrane and the Ag/AgCl electrode [2].

To prepare the solid-state pH sensor, the ion selective poly(*n*-butylacrylate), p(*n*BA) film was deposited by placing a cocktail containing various membrane components on top of the hydrated

pHEMA inner layer followed by photocuring the mixture [12]. The cocktail was prepared by mixing 44.7mg of monomer *n*BA, 0.1wt% of the cross-linker 1,6-hexanedioldiacrylate (HDDA), 0.1mg photoinitiator DMPP and the required amount of the hydrogen ionophore and lipophilic salt NaTFPB as shown in Table 1. The membrane cocktail was then photocured for 3 min to yield a 0.5 mm thick p(*n*BA) film using an UV exposure unit under a nitrogen atmosphere. Three pH sensors were prepared using this procedure for each formulation shown in Table 1.

Sensor evaluation

The responses of various pH sensors depicted in Table 1 were assessed in an electrochemical cell setup, with a double junction reference of Ag/AgCl electrode containing an internal reference solution of 0.1M Tris-HCl (pH 7) and 1M lithium acetate gel as a bridge electrolyte. Both the reference electrode and the pH sensor, which were connected to an Orion ion meter, were exposed to buffers ranging from pH 4-7. The potential of the cell (electromotive force, emf) (mV) was recorded when a stable value was reached. The emf response of the test cell was then plotted against the logarithmic concentrations of the test solutions according to the Nernst Equation. All the measurements were conducted at room temperature (30±2°C).

The effect of the Tris-HCl buffer concentration on the response of the sensor was also evaluated by using Tris-HCl concentrations of 0.1, 0.05, 0.01 and 0.005M. All the sensors were evaluated in the range of pH 4-10 and the pH value of each buffer solution was measured with Ecomet pH electrode before and after a sensor has been tested. Interference study was carried out by employing the fix interference method (FIM) [19] with 0.1M of chlorides of various cations, e.g. potassium, sodium, lithium, calcium and magnesium as interference cations.

Analysis of real samples

All real samples were measured in triplicates with three different solid-state pH sensors. The pH measured by the solid-state pH sensor was then compared with pH measurement of the same sample from a conventional pH glass electrode (Ecomet). The difference in the measurements were tested using t-test at $\alpha=0.05$.

For environmental samples such as seawater, they were collected from Port Dickson, Malaysia. Sewage sample was collected from a sewage treatment plant in Universiti Kebangsaan Malaysia and tested without any pretreatment. Clinical samples such as urine were collected from two persons (urine 1 & urine 2) in the morning. The samples were autoclaved before used for sensor study. For food samples such as milk, three types of consumer packed milk were purchased, which included low fat

Table 1 : The response of solid-state pH sensors with different compositions of hydrogen ionophore and NaTFPB in poly(nBA) films.

Sensor	Hydrogen ionophore (% by weight)	NaTFPB (mg) (% mol relative to ionophore)	Response slope (mV/decade)
EI25L00	5.0	0	Slight response
EI25L05	5.0	0.2 (5)	39.8±10.1
EI50L05	10.0	0.4 (5)	39.0±2.0
EI25L10	5.0	0.4 (10)	48.7±1.6
EI50L10	10.0	0.8 (10)	52.4±1.4
EI25L15	5.0	0.6 (15)	47.1±4.2
EI50L15	10.0	1.3 (15)	45.9±1.0
EI50L12	10.0	1.0 (12)	52.6±3.5
EI25L25	5.0	1.1 (25)	42.8±8.5
EI00L15	0	1.3	Slight response

milk, low fat with high calcium milk and full cream milk. No pretreatment of milk samples was carried out before they were used for sensor study. For cheese samples, consumer packed cheddar cheeses was purchased. A slice of cheddar cheese of the appropriate weight was hard-pressed and then added to a known volume of distilled water. The suspension was stirred and gently heated for about 15 min until a cheese emulsion was formed. Samples with 11 wt% and 54 wt% of cheese based on weight of cheese:total weight of cheese and water were prepared in this manner.

Results and Discussions

Effect of membrane compositions on sensor response

The addition of lipophilic salts for ion-selective sensor based on polymeric membranes is to improve the capability of the membrane to induce permselectivity that will lead to good sensor performance. Tetraphenylborate derivatives are commonly used as lipophilic anionic sites to improve the cation permselectivity if the ionophore has poor extraction capability and also to reduce the anion interference and lower the membrane resistance [20-25]. Among the lipophilic salts, tetrakis [3,5-bis(trifluoromethyl)phenyl]borate (TFPB) is shown to be the chemically most stable tetraphenylborate anion in the membrane phase [21, 22]. Thus, NaTFPB has been chosen to be the lipophilic anionic site in this study. The leaching of lipophilic salts can be reduced with the present of ionophore in the membrane [22].

An ionophore forms reversible and relatively strong complex with a specific target ion. Therefore, hydrogen ionophore has the ability to transport H^+ into the sensor membrane from the bathing electrolyte [14, 16, 23, 24, 26-28]. High potential

energy from the dipole-ion interaction between lipophilic anionic sites (e.g. from NaTFPB) in the membrane induces the transfer of the ion-carrier complex through the test solution-membrane boundary. This ion-carrier complex moves through the membrane as a unit, and unloads the hydrogen ion at the opposite exiting membrane interface, and thus a high concentration of free carrier is then built up in the membrane for further ion transport [2, 16]. This enables equilibrium exists between free carrier and hydrogen ions and the ion-carrier complex reaction is reversible [23]. In this study, tridodecylamine, a neutral ion carrier is chosen as the hydrogen ionophore, which acts as a complexing agent that is entrapped in the acrylic membrane that enhances the permselectivity of H^+ sensor.

In Table 1, the response of the solid-state sensor appears to be dependent on the amount of NaTFPB. This can be seen by comparing the response of sensors with no NaTFPB (EI25L00) with sensors containing 5 mol% of NaTFPB + 5 wt% ionophore (EI25L05) and sensor with the same amount of NaTFPB but 10 wt% of ionophore (EI50L05). Both EI25L05 and EI50L05 yielded similar response slopes (Table 1 and Fig 1) even though the amount of ionophore has increased from 5 to 10 wt%. But when the amount of NaTFPB was increased to 10 mol% (i.e. sensors EI25L10 and EI50L10), an increase in the ionophore content leads to improvement in the response slope to 52.4 mV/decade. Even when NaTFPB is increased further to 12 mol% (sensor EI50L12) the slope remains as 52.6 mV/decade. However, when the amount of NaTFPB exceeded 15 mol% (sensors EI25L15, EI50L15 and EI25L25), the response slope decreases. Thus the optimum membrane components are 10 wt% of ionophore and 10-12 mole% of NaTFPB. Ion

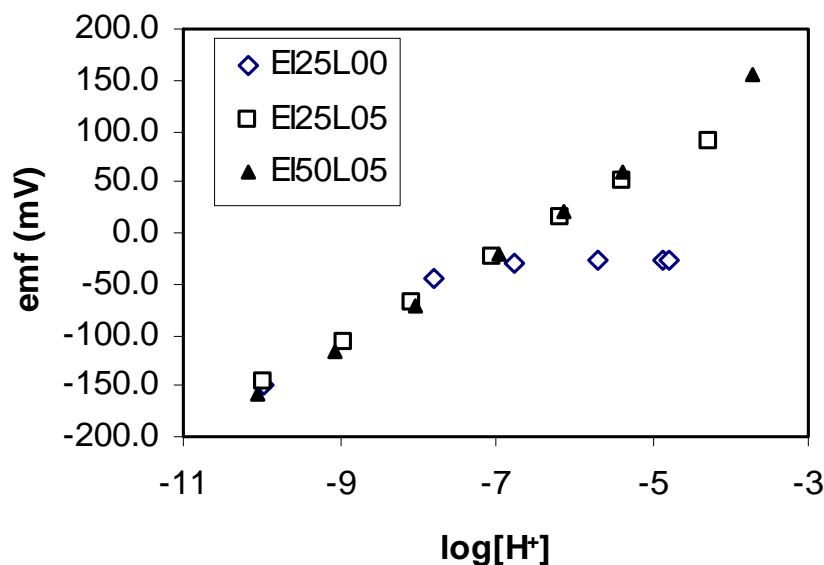


Figure 1 : The response of sensors EI25L00, EI25L05 and EI50L05 over the range of pH 4 –10 in 0.1M Tris-HCl buffer.

selective-electrodes with slopes higher than 55mV/pH at 25°C can be considered as demonstrating near Nernstian response [31]. In this work, sensor with membrane components of 10 wt% ionophore and 12 mol% NaTFPB (i.e. sensor EI50L12) have slopes close to 55 mV/pH (within experimental error) was chosen for further studies.

The effect of the amount of ionophore on the sensor response can be seen by comparing the sensors with no ionophore (sensor EI00L15) and 10 wt% of ionophore (sensor EI50L15) (Table 2 & Fig 2). Clearly in the presence of the ionophore, the sensor showed higher response to pH compared with sensor membrane that did not have any ionophore. The slight response of the sensor without ionophore is due to the non-specific interaction of the lipophilic anionic sites with cations in the bulk solution.

Effect of buffer concentration pH sensor response

Tris-HCl is a buffer useful for pH control in the physiological range [29] and can be used as a background electrolyte that has no interfering alkaline cations [1]. The effect of Tris-HCl concentrations on the response of the solid-state pH sensor was studied with Tris-HCl concentrations of 0.1, 0.05, 0.01 and 0.005M. Investigating two pH sensors in these buffer concentrations demonstrated that the sensors gave similar response slopes, only changes of about 5 mV/pH (Table 2) were observed even though the concentration of the buffers changed by 10-200 folds. Thus, the sensor response did not depend on the Tris-HCl concentration from 0.005-0.1 M.

Table 2. : The response of solid-state pH sensors in Tris-HCl buffer solutions of different concentrations.

Sensor	Tris-HCl (M)	Slope (mV/pH)
EI50L10	0.1	52.4±1.4
EI50L10	0.01	53.3±0.4
EI50L10	0.005	51.3±1.3
EI50L12	0.1	52.6±3.5
EI50L12	0.01	56.5±1.2

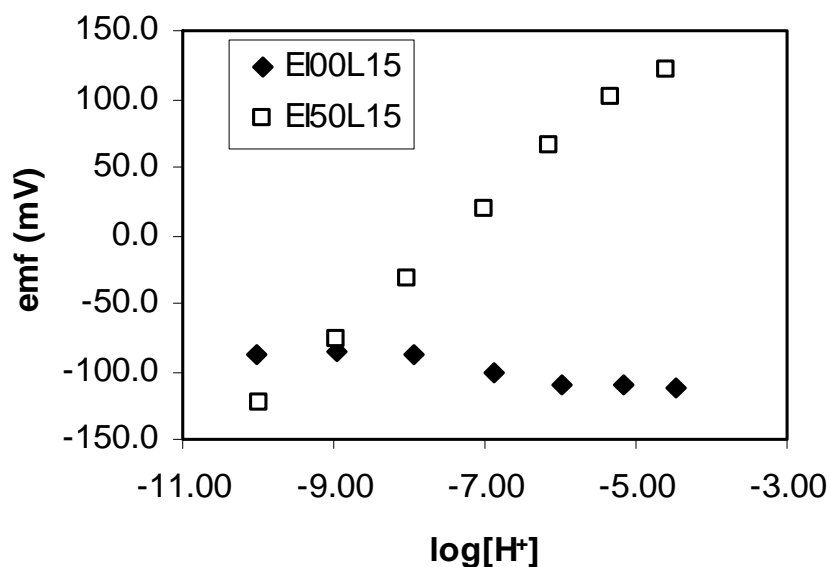


Figure 2 : The responses solid-state pH sensors with (EI50L15) and without ionophore (EI00L15) over the pH range of 4 – 10 (0.1M Tris-HCl).

Interference behavior of solid-state pH sensor

The selectivity of the pH sensors in the presence of various major interference cations is shown in Table 3. The response slopes varied between 54.4-58.9 mV/decade. This is similar to data reported in Table 2 where no other cations were added during the studies. Hence, the presence of 0.1M of other cations did not exert observable interference on the sensor response and the sensor is selective to hydrogen ions even in the presence of high level of other cations.

Reproducibility and repeatability of the solid-state pH sensors

The reproducibility and repeatability of the fabricated solid-state pH sensors are satisfactory with the response slopes showed little variation (relative standard deviations (RSD) < 2%). (Table 4). The calibration curve of three solid-state pH sensors also yielded good reproducibility (Figure 3). This demonstrates that the process of fabrication via photocuring can give sensors of consistent analytical performance.

Table 3 : The performance of solid-state pH sensors in the presence of 0.1 M of other cations.

Cations (0.1M)	Slope (mV/decade)	R ²	Linear range (pH)	*Estimated selectivity coefficient $\log K_{H-M}^{pot}$
K ⁺	54.9	0.9984	3.38-9.75	<-8.75
Na ⁺	55.1	0.9998	4.01-9.76	<-8.76
Li ⁺	55.1	0.9998	4.00-9.82	<-8.82
Ca ²⁺	55.8	0.9994	3.92-9.93	<-9.43
Mg ²⁺	56.8	0.9989	3.91-9.84	<-9.34

* Calculated by using fixed interference method based on the lowest concentration of hydrogen ion used in each solution containing 0.1M of interference cations.

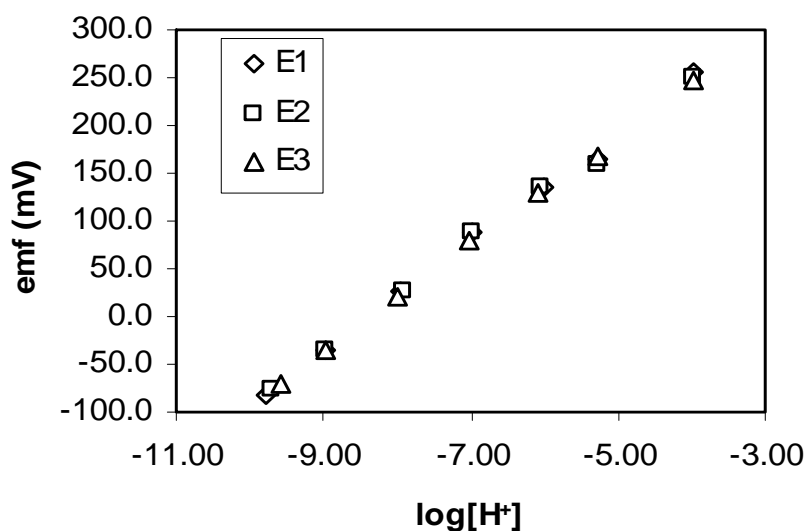


Figure 3 : The response of three pH sensors fabricated from photocuring technique over the pH range of 4 –10 (in 0.01M Tris-HCl buffer).

Table 4 : The reproducibility and repeatability of pH sensors fabricated from photocuring method.

	Linear range (pH)	Slope (mV/decade)	RSD (%)
Reproducibility (n = 15)	4 - 10	56.5±1.0	1.8
Repeatability (n = 3)	4 - 10	56.8±0.5	0.9

Application of solid-state pH sensors in real samples

The measurement of pH is essential in water quality assessment. It is used to determine the solubility and bioavailability of chemical constituents, e.g. nutrients and heavy metals. Besides, most of the biological activities in natural water are affected by the pH condition [32]. The pH of seawater measured by the solid-state pH sensor was slightly lower than that measured by a conventional glass electrode (Table 5). This may be due to the high concentration of interference ions such as potassium and sodium in the seawater matrix. The interference is unlikely to be caused by the loss of selectivity of the ionophore but attributed to the effect of the added anionic sites. The hydrogen ionophore triiododecylamine has a high complexation constant for proton and forms complex preferentially with hydrogen ions [23]. Therefore, the presence of high level of potassium or sodium ions in the seawater is unlikely to affect the complexation behaviour of the hydrogen ionophore. The fixed anionic sites present, on the other hand, may interact with the cations in the seawater and this may affect the equilibrium of the free ionophore and ionophore-

hydrogen ion complex in the membrane. And this leads to changes in the response toward hydrogen ions. On the other hand, domestic sewage, which has relatively lower ionic content when compared to seawater did not suffer interference by cations and thus demonstrated no significant difference in the two pH values measured by both methods (Table 5).

The pH of the human urine is an indication of how the body maintains the proper pH of the blood, which is 7.35-7.45 [33]. When the pH of the blood is low, the kidney reacts by excreting more acid in the urine and the pH of urine becomes more acidic until the blood pH returns to normal. Therefore, the pH of urine is an important indicator for the proper functioning of the human body via regulation of buffering salts and hormones [33]. The normal composition of urine consists of cations such as sodium (0.4%) and ammonium (0.05%) [34], which may interfere with the solid-state pH sensor response. But the data in Table 5 demonstrated that such interference is negligible because the pH values measured by glass electrode and the solid-state pH sensor are not significantly different.

Table 5 : A comparison of results for the pH measurements in some real samples by using the solid-state pH sensor with poly(nBA) membrane and conventional pH glass electrode and the % difference between the two methods.

Sample	Solid-state pH sensor (n=3)	Glass pH electrode (n=3)	Difference (%)
Seawater	7.52±0.03	7.98±0.04	5.8**
Sewage	7.78±0.02	7.99±0.04	0.3
Urine 1	6.62±0.14	6.71±0.08	1.3
Urine 2	5.98±0.15	6.09±0.01	1.9
Low fat milk	6.55±0.13	6.49±0.02	0.9
Low fat milk (high calcium)	6.42±0.10	6.38±0.00	1.9
Full cream milk	6.65±0.03	6.65±0.01	0
Cheddar cheese (11% wt)	6.01±0.11	5.95±0.05	1.0
Cheddar cheese (54% wt)	5.64±0.11	5.65±0.02	0.2

** t-test indicates significant difference at $\alpha=0.05$.

The pH value of cheese is essential in the determining the quality of Cheddar cheese [27, 35-38]. The changes of pH during cheese manufacturing are an indication of acid development in the cheese products by lactic acid bacteria added to the milk [27, 35]. The main composition of cheese is protein, fat, and minerals such as calcium, magnesium and sodium ions [35, 37]. These contents may cause interference to the solid-state pH sensor. The high level of lipids and protein in cheese may result in the extraction of neutral lipids or peptides into the hydrophobic polymer membrane and this can lead to membrane fouling [27]. A comparison of the pH measured by the solid-state pH sensor and glass electrode demonstrated no significant different between the two pH values determined. This is also true even the amount of cheese in the pH determination was increased to more than 50 wt% (Table 5). Thus, at this level of cheese content, membrane fouling by lipid or protein did not occur. The direct measurement of pH on various types of milk using the solid-state pH sensor also showed similar values when compared to that determined by glass electrode (Table 5). Thus the solid-state pH sensor designed in this study is suitable for measuring pH in dairy products.

Conclusion

This study has shown that photocurable poly(nBA) membrane can be used to fabricate functional solid-state pH sensor that required no added plasticizer. When various added components of the membrane are optimized, the performance of the solid-state pH sensor is comparable to other plasticized membrane matrices used for pH sensors reported in the literature. The solid-state pH sensor fabricated here is particularly suited for the analysis of samples with varying matrices, particularly that

contained fats and protein. This shows that the hydrophobic membrane matrix of poly(nBA) does not interact strongly with this sample components, which can normally cause membrane fouling.

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