The behaviour of polyaniline-coated PVC membrane based on 7, 16-didecyl-1, 4, 10, 13-tetraoxa-7, 16-diazacyclooctadecane for pH measurements in highly acidic media

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Abstract. Polyaniline(PANI) chemically coated on poly(vinyl chloride) (PVC) membrane based on a neutral carrier 7,16-didecyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (kryptofix 22 DD) as the active component has been developed for determination of pH values ranging from pH 0.1–1. The effect of experimental parameters such as membrane composition, nature and amount of plasticizer, lipophilic additives and thickness of PANI film on the potential response of the pH electrode was investigated. The electrode has an apparent Nernstian response slope of $54.5 \pm 0.4 \text{ mV pH}^{-1}$ (at 20°C). The equilibrium water content of the electrode was determined in pure water and NaCl solution ($I = 0.1 \text{ mol Kg}^{-1}$). The electrode had low electric resistance, good potential stability and reproducibility ($\pm 1.5 \text{ mV}$, $n = 10$). It has a rapid potential response to changes of pH (15 s). The excellent performance in terms of linearity, stability and fast response makes this device suitable for pH measurements in highly acidic media.

Keywords. Polyaniline; 7,16-didecyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane; poly(vinyl chloride) membrane; hydrogen ion-selective electrode.

1. Introduction

The pH measurements are generally carried out by use of glass electrodes. These electrodes have become very popular to their selectivity, reliability and dynamic pH range. Although pH-sensitive glass electrode has distinguished response characteristics and has been in use for such a long period, it has certain setbacks such as high resistance, fragility, instability in hydrofluoric acid or fluoride solutions and unsuitability to serve as a microelectrode for biological applications.^{1–3} Classical liquid exchangers have been used for the preparation of hydrogen ion-sensitive poly(vinyl chloride) (PVC) membranes with limited success.^{4,5} Neutral carriers showed much more promising characteristics for the preparation of PVC pH electrodes and have been studied by several investigators.^{6–8} Fouskaki *et al.* have reported liquid polymeric membranes based on 3-hydroxypicolinic acid derivatives for measurement of subzero pH values.⁹ Hydrogen ion-selective electrodes using calixarene derivatives as

neutral carriers were also prepared such as 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetracyanomethoxy calix-[4]arene,¹⁰ calix[4]-aza-crowns,¹¹ p-tert-butyl calix[4] arene-oxacrown-4,¹ all of which showed sensitivity at $\text{pH} > 2$. Some hydrogen ion selective membrane electrodes based on amines as neutral carriers were also prepared with similar pH sensitivity.^{12–15}

On the other hand, robust, reliable, and maintenance-free ion sensors are highly desirable for demanding applications such as on-line process analysis and clinical analysis. One approach toward durable ion selective electrodes (ISEs) is to produce all-solid-state electrodes without any internal filling solution. However, high potential stability is a prerequisite for obtaining reliable sensors. Nikolskii and Materova identified three conditions that should be fulfilled in order to obtain a stable electrode potential for ISEs with a solid internal contact:¹⁶ (i) Reversibility and equilibrium stability of transition from ionic to electronic conductivity. (ii) Sufficiently high exchange currents in comparison with the current passed during measurement. (iii) Absence of side reactions parallel to the main electrode reaction. The potential stability of the all-solid-state electrodes can be improved by using a protecting layer with suitable ion-exchange properties on the ionically

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conducting ion-selective membrane. A promising approach in this respect is to use an electroactive polymer (conducting polymer or redox polymer) in combination with carrier-based ion-selective membranes.¹⁷ On the basis of their ion-exchange properties, conducting polymers fulfill at least stability condition (i) presented above.^{18,19}

The development of polymer blends resulted in the improvement of their mechanical properties and the application of polyaniline (PANI) and polypyrrole in electrochemical devices has been reported.^{20,21} Much work has been devoted to the study of charge transport through polymeric materials containing extended JT-conjugated backbones, such as polypyrrole, polythiophene and polyaniline.²² A literature review shows that there are many reports on the use of PANI as conducting polymer matrix in the development of electrochemical sensing devices. PANI coated Pt, Pd and graphite electrodes have been studied.²³ Their potential relationship to pH follows the same principle as the pH glass electrode. The non-protonated form of polyaniline was used for pH 6.8 to 1.2 and the protonated form of polyaniline was used for pH 6.8 to 13.²⁴ PANI films can be obtained directly on an ultra-microelectrode through the anodic electropolymerization of the monomer through successive potential cycles, and a linear relationship with pH is observed in the range 3–9 with a slope of 60 mV per pH unit.²³ The behaviour of a polyaniline solid contact pH selective electrode based on N,N',N,N'-tetrabenzylethane diamine ionophore was investigated by Han group.²⁴ The linear dynamic range of this electrode was observed (pH 3.5–11.94) with a Nernstian slope of 52.1 mV pH⁻¹. Han *et al.* also prepared a hydrogen ion selective polyaniline solid contact electrode based on dibenzylpyrenemethylamine ionophore for highly acidic solutions (pH = 0.5).²⁵ This group also investigated the presence of other neutral carriers such as N,N' dialkylbenzylethylenediamine and tribenzylamine in a PVC membrane with polyaniline solid contact.^{26,27} Zine *et al.* suggested a neutral conductive polymer, polypyrrole doped with cobaltabis(dicarbollide) ions, as an internal solid contact layer for pH measurements with linear response over the pH range of 3.5–11 (slope 52.2 mV pH⁻¹).²⁸

The chemistry of PANI is a little intricate, due to the existence of different acidic functions and oxidation states. There are three oxidation states and each redox couple corresponds to a 2e exchange. The less oxidized state, leucoemeraldine (LEB), the intermediate state emeraldine (EB) and the most oxidized state, pernigraniline (P) are insulating. The only conductive form is the intermediate emeraldine salt (ES).²³ Imine sites of the EB form are easily protonated, with a

striking insulator–conductor transition, induced due to the appearance of polarons in the lattice, while the number of π -electrons remain constant. As a consequence, new optical, conducting, and paramagnetic properties appear in the ES. These properties make PANI to be successfully used as a sensor.^{29–31}

The surface properties of thin PANI films, such as the hydrophilicity and surface morphology, can improve the properties of the various matrices, in particular the traditional PVC membranes, and make them more useful in the field of analytical chemistry.³² Polyaniline (scheme 1) is one of the most studied conducting polymers due to its good stability, easy preparation and low cost of reactants.

Due to the pH-dependent PANI (emeraldine) salt–base transition, polyaniline has been successfully used as an additive to the typical ion-selective membrane based on PVC or silicone, but any of them were never applied in pH < 1.^{32,33} With regard to the above-mentioned features, a polyaniline film should act simultaneously as a new additive into a membrane electrode and as a membrane component affecting the ion transport. In this work, we report the effect of PANI deposition on the potentiometric behaviour of a membrane pH electrode based on a neutral carrier 7,16-didecyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (kryptofix 22 DD, scheme 2) toward hydrogen ions in highly acidic media (pH < 1). The response time, the lifetime of the electrode and its selectivity against some anions and cations were investigated.

2. Experimental

2.1 Reagents and solutions

Aniline and tetrahydrofuran (THF) were purified by vacuum distillation. Redistilled water and analytical-reagent grade reagents were used throughout. High-

Scheme 1. Polyaniline (emeraldine) salt exists in acidic media and it deprotonated to PANI (emeraldine) base in alkaline media. HA is an arbitrary acid.

Scheme 2. Chemical structure of kryptofix 22 DD used as ionophore.

molecular weight poly(vinyl chloride) (PVC), bis(2-ethylhexyl)sebacate (DOS), dibutyl sebacate (DBS), dibutyl phthalate (DBP), acetophenone (AP), ammonium persulphate, potassium tetrakis(*p*-chlorophenyl) borate (KTpClPB), oleic acid (OA), 7,16-didecyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (kryptofix 22 DD), and tridodecylmethylammonium chloride (TDDMACl) were purchased from Fluka or Merck. The solutions were prepared in order to determine the effect of mono, di and trivalent ions on the electrode response by the use of fixed interference method (FIM), and modified separate solution method (MSSM). A series of calibration solutions were prepared in pH range 0.1–1.0 by dilution from HCl 12 mol L⁻¹. During this work, buffer solutions were prepared from HIO₃/KIO₃ ($K_a = 1.7 \times 10^{-1}$) for the determination of pH sensitivity and potentiometric selectivities of the respective electrode.

2.2 Membranes

In the present study, 1.2 mL THF was used to dissolve a mixture composed of the active component kryptofix 5.7% (3.6 mg), the plasticizer AP 41.2% (26.2 mg) and PVC 53.1% (33.8 mg). Solutions of the resultant mixtures were placed on a glass plate, and THF was evaporated at room temperature.

2.3 Polyaniline deposition

The deposition of a PANI film was performed by soaking an appropriate PVC membrane in a freshly prepared mixture of aniline hydrochloride (1 mol L⁻¹) and ammonium persulphate (0.50 mol L⁻¹) as oxidant. During the aniline polymerization, a thin green PANI film with a thickness of about 100–200 nm was grown on both sides of the plasticized PVC membrane surface.³³ The PANI-coated PVC membranes were rinsed with 0.20 mol L⁻¹ hydrochloric acid and dried in air. The oxidation of aniline in an acidic aqueous medium

produces, at first, aniline oligomers. These are more hydrophobic than the original anilinium cations. They have a tendency to separate from the aqueous medium, e.g., by adsorbing themselves at available surfaces in contact with aqueous reaction mixture. The adsorbed oligomers have a higher reactivity toward initiating the growth of PANI chains. This is the principle of heterogeneous catalysis, which postulates that the reactivity of adsorbed molecules may be increased because of the altered electron density distribution. It has indeed been observed experimentally that the polymerization at the surfaces precedes the polymerization in the bulk of the reaction mixture. The first PANI chain anchored at the surface produces a nucleus of the future film. The polymerization of aniline is auto-accelerated. This means that new oligomers are thus born and adsorbed close to the nucleus, and stimulate the growth of new PANI chains. The PANI chains forming a film thus proliferate along the surface and for steric reasons, are oriented preferentially perpendicularly to the support.^{34–36}

2.4 Electrode preparation and EMF measurements

A part of membrane was cut as circle, glued with a PVC/THF paste, and mounted in the electrode body for EMF measurements. An aqueous solution of 1×10^{-2} mol L⁻¹ HCl was used as filling of the electrode. PANI-coated PVC pH-electrode prepared was conditioned in 1×10^{-3} mol L⁻¹ HCl solution for 12 h. The cells used for mV measurements were of the type Hg; Hg₂Cl₂, KCl (sat'd) | sample solution || membrane || HCl 1×10^{-2} mol L⁻¹ | Hg; Hg₂Cl₂, KCl (sat'd).

2.5 Equilibrium water content

The equilibrium water content (EWC) of PVC membranes based on AP as plasticizer was evaluated using the gravimetric method.³⁷ Dry membranes weighing about 100 mg (w_1) were immersed in the appropriate soaking medium (H₂O, 10^{-1} mol L⁻¹ NaCl) for 5 days and the swollen membranes were blot dried with a paper towel and immediately weighed (w_2). Then, the swollen membranes were dried at room temperature to a constant weight (w_3). The EWC values were calculated using the following equation:

$$\text{EWC}(\%) = [(w_2 - w_3)/w_2] \times 100. \quad (1)$$

The loss of plasticizer (LP) from the membrane into the water phase was evaluated from the difference between w_1 and w_3 .

Table 1. Effect of the membrane composition on the slope of the PANI-coated PVC membrane pH electrode (PVC/plasticizer ratio = 1.3).

Electrode number	Membrane composition (%)			Slope $\pm$ ts/ $\sqrt{N}$
	Ionophore	AP	PVC	
1	—	42.2 (25.5 mg)	57.8 (35 mg)	35.1 $\pm$ 0.8
2	1.6 (1.0 mg)	41.4 (25.5 mg)	57 (35 mg)	38.2 $\pm$ 0.7
3	3.3 (2.0 mg)	41 (25 mg)	55.7 (34 mg)	42.7 $\pm$ 0.8
4	5.7 (3.6 mg)	41.2 (26.2 mg)	53.1 (33.8 mg)	54.5 $\pm$ 0.9
5	5.7 (3.5 mg)	32 (19.5 mg)	62.3 (38 mg)	41 $\pm$ 1
6	6.0 (5.0 mg)	59.5 (50 mg)	34.5 (29 mg)	49.2 $\pm$ 1.2

2.6 Selectivity measurements

Selectivity coefficients were determined using fixed interference method (FIM) and modified separate solution method (MSSM). The FIM requires determination of the primary ion response in the presence of a constant background of interfering ions. Selectivity coefficients are then calculated as:³⁸

$$K_{I,J}^{Pot} = \Delta a_I / (\Delta a_J)^{(z_I/z_J)}, \quad (2)$$

where a_I represents the activity of primary ions at the detection limit and a_J is the activity of the interfering ions in the sample background. In MSSM, the potential of a solution containing the primary ion and one the interfering ion, are measured independently. Using the emf values obtained, the potentiometric selectivity coefficients, or Nikolskii coefficients as it is sometimes called, can be calculated using the following equation:³⁸

$$\log K_{I,J}^{Pot} = \frac{(E_J - E_I) z_I F}{2.303RT} + \log \left(\frac{a_I}{a_J^{z_I/z_J}} \right), \quad (3)$$

where $\log K_{I,J}^{Pot}$ is the potentiometric selectivity coefficient, E_I and E_J , Z_I and Z_J and a_I and a_J are the emf values, valances and sample activities for a primary ion I and an interfering ion J , respectively. F , R and T are Faraday's constant, the universal gas constant and the absolute temperature, respectively.

3. Results and discussions

3.1 Effect of membrane composition

In the first series of studies, the effect of the ionophore ratios upon the response of the electrode was investigated by changing its content to, 0%, 1.6%, 3.3%, 5.7%, 6% with known PVC/AP ratio = 1.3 ($m \cdot m^{-1}$). In the second series of studies, the effect of the plasticizer was observed by keeping the content of the ionophore at 5.7% and using DBS, DBP, and DOS instead of AP. The effect of the lipophilic anion was evaluated by the addition of lipophilic salts: KTpCIPB, OA, and TDDMACI at a concentration of 4.4% to one of the best performing membranes containing 5.7% ionophore, 41.2% AP and 53.1% PVC (PVC/plasticizer mass ratio of 1.3). The results obtained from the electrode prepared with the membrane having a PVC/plasticizer ratio of 1.3 are given in tables 1 and 2.

The slopes of the electrodes prepared by the use of DOS, DBP, and DBS as plasticizer were found to be quite low (approximately 39–42 mV pH^{-1}) (figure 1). This has led us to the conclusion that the type of plasticizer employed has a marked effect upon the performance of the PANI-coated PVC membrane electrodes. From four plasticizers tested, AP showed the best results than others, probably because of its more polarity and dielectric constant ($\epsilon = 17.5$).

Table 2. Effect of the lipophilic anions on the slope of PANI-coated PVC membrane pH electrode (PVC/plasticizer ratio = 1.3).

Slope	Lipophilic anion (%)			PVC (%)	AP (%)	Ionophore (%)	No.
	TDDMACI	KTpCIPB	OA				
40.1	—	—	4.4 (2.8 mg)	50.5 (32 mg)	39.4 (25 mg)	5.7 (3.6 mg)	1
41.0	—	4.4 (2.8 mg)	—	50.5 (32 mg)	39.4 (25 mg)	5.7 (3.6 mg)	2
40.2	4.4 (2.8 mg)	—	—	50.5 (32 mg)	39.4 (25 mg)	5.7 (3.6 mg)	3

Figure 1. Calibration curves of PANI-coated PVC pH electrode with a membrane containing 41.2% plasticizer, 53.1% PVC and 5.7% kryptofix 22 DD: (●) AP, (○) DOS, (△) DBS, (▲) DBP.

It is obvious that the decrease in concentration of the kryptofix 22 DD in membrane results in demolition slope (approximately $35\text{--}42\text{ mV pH}^{-1}$). The results showed that the membrane without ionophore has low sensitivity with slope of 35.1 ± 0.8 compared to 54.5 ± 0.9 in the presence of 3.6% of ionophore. Accordingly, the presence of ionophore is essential to achieve good response and the PANI itself does not show an appropriate Nernstian response. The effect of ionophore is attributed to its macrocyclic structure and oxygen atoms that coordinate the hydrogen ions presented in the PANI film. In our study with the membranes prepared using potassium tetrakis(*p*-chlorophenyl)borate, oleic acid and tridodecylmethylammonium chloride as lipophilic reagents it was found that the sensitivity towards the hydrogen ion showed a significant decrease (table 2). The effect of the lipophilic anion in the hydrogen ion sensitive membrane prepared by the use of kryptofix 22 DD may be inherent to the structure of the ionophore. In fact, this diminished slope could be attributed to the opposite cation residing in the open cavity surrounded by the oxygen and nitrogen atoms, and the lipophilic anion getting close to the opening, to form an ion pair; thereby making the ionophore impossible, for the protons, to penetrate into.

The effect of the conditioning upon the performance of the electrode was investigated by the use of two electrodes with the same composition. One of the electrodes was conditioned in $1.0 \times 10^{-3}\text{ mol L}^{-1}\text{ HCl}$ and the other in pure water for 12 h. The conditioned electrodes were then placed in the electrochemical cell described above and the potentials were recorded. The results obtained reveal

Figure 2. Dynamic response time of the PANI-coated PVC membrane electrode for step change in pH (a) 1, (b) 0.8, (c) 0.5, (d) 0.2 (membrane no. 4).

that the performance and the lifetime of the electrode conditioned in pure water were much lower than that of the electrode conditioned in acid solution. Therefore, the electrodes were conditioned in $1.0 \times 10^{-3}\text{ mol L}^{-1}\text{ HCl}$ for 12 h prior to each experiment.

3.2 Working range and the slope of the electrode

Using a series of buffer solutions in the range of pH 0.1–1 as analytes the potential of the cell was measured. The potentials measured were plotted against the pH values to obtain the calibration curves. Figure 1 shows the calibration curves of the electrodes made by the use of four different plasticizers. As seen from figure 1, the linear working range of the AP containing electrode is better than those of DOS, DBS and DBP containing electrodes. The slope and the linear working range of the electrode prepared with 5.7% kryptofix 22 DD, 41.2% AP and 53.1% PVC were found to be 54.5 mV pH^{-1} and the pH was 0.1–1. The proposed pH

Figure 3. The lifetime of PANI-coated PVC membrane electrode (membrane no. 4).

Table 3. Selectivity coefficients of the proposed hydrogen ion-selective electrode based on kryptofix 22 DD.

Interfering ions	$\log K_{I,J}^{Pot}$		Interfering ions	$\log K_{I,J}^{Pot}$	
	FIM	MSSM		FIM	MSSM
Li ⁺	−1.8	−2.7	Pb ²⁺	−2.7	−3.7
Na ⁺	−1.6	−2.2	Ni ²⁺	−3.0	−3.3
K ⁺	−1.9	−2.5	Co ²⁺	−3.2	−4.1
Mg ²⁺	−2.5	−3.1	Cr ³⁺	−2.5	−2.9
Ca ²⁺	−2.3	−3.0	Zn ²⁺	−2.8	−4.5
Mn ²⁺	−2.8	−3.6	Bi ³⁺	−3.0	−4.3

electrode had good potential stability and reproducibility (± 1.5 mV, $n = 10$). In fact, the use of PANI film in combination with carrier-based ion-selective membrane had overcome many of the potential stability problems.

3.3 The effect of the reinforcing and thickness of PANI film

The potential measurements from pH 1 to 0.1 indicated slow protonation or adsorption of H⁺ on PANI. With the increase in the acidity of solutions, protonation of PANI as well as its conductivity will increase; and as the electrode was washed with distilled water before each potential measurement, there were always some unprotonated nitrogen in PANI which could become protonated and create a potential change. On the other hand, the slight difference in the slopes was possibly due to the difference in the firmness with which the PANI film was coated onto the membrane surface and to the smoothness of the polyaniline surface, smoother surface of the polyaniline film deposited on the membrane showed more sensitivity,²⁴ evidently membrane without PANI film showed strongly decreased slope (35.15 mV pH^{−1}). This survey indicated the role of reinforcing PANI film on sensitivity and selectivity of the electrode by conducting hydrogen ions toward ionophore located into the membrane. The time of deposition of PANI film on membrane was investigated; the best time for coating of PANI on PVC membrane was 3 h. We assume that with increasing thickness of the PANI coating, the adjustment of the equilibrium at the surface will be limited to some extent and diffusion and retention of ions must also be considered.

3.4 Response time and lifetime of the electrode

The time for the electrode to reach a stable potential after it was immersed into the calibration solutions (response time) was recorded starting from low pH solution to high pH ones. The response time of the

electrode was found to be several seconds (approximately 15 s) (figure 2).

The lifetime of the electrode was determined by reading its potentials and plotting the calibration curves for a period of 60 days. Even at the 60th day, the slope of the electrode was observed to show no significant change (figure 3). This shows that the lifetime of the electrode prepared by this method was longer than 60 days.

3.5 The selectivity of the electrode

It is known that the cations such as lithium, sodium and potassium narrow in the lower and anions such as bromide, iodide and thiocyanate in the upper limit of the working range of the hydrogen ion-selective electrodes. In short, many ionic impurities are expected to reduce the working range of the electrode.^{13,39} With respect to this knowledge, the effect of alkaline cations and some other ions on the electrode performance was evaluated by the fixed interference method (FIM). However, it is easily demonstrated that FIM is highly dependent on obtaining Nernstian response slopes for interfering ions. Because of the flux of primary ions from the backside of the membrane in conventional electrode configurations (inner filling solution $a_I \geq 10^{-3}$ mol L^{−1}) and the subsequent leaching of primary ions into the sample at the sample-membrane phase boundary, sub-Nernstian response slopes are often observed when measuring solutions containing interfering ions. This is because the primary ion, I , and interfering ion, J , are both potential-determining.

Sub-Nernstian response slopes invalidate $K_{I,J}^{Pot}$ values that are reported if they were obtained using the classical separate solution method (SSM) or the fixed

Table 4. Equilibrium water content (EWC%) and loss of plasticizer (LP%) from proposed pH electrode.

	EWC (%)	LP (%)
In H ₂ O	28%	0.06%
In 10 ^{−1} mol L ^{−1} NaCl	3%	0.21%

Figure 4. Electric resistance of PANI-coated PVC membrane electrode at different conditioning times (membrane no. 4).

interference method (FIM), which both require that all ions measured exhibited Nernstian behaviour. In recent years, a modified separate solution method (MSSM) has been introduced that allows unbiased potentiometric selectivity coefficients to be determined.⁴⁰ In contrast to previous methods, MSSM has a significantly different experimental protocol whereby the inner filling solution of the ISE contains a high concentration of an interfering ion rather than the primary ion and the screening of interfering ions occurs in the order of increasing interference prior to obtaining the emf values for the primary ion.⁴¹ With respect to this knowledge, the effect of Li^+ , Na^+ , K^+ and some other cations on electrode response and their selectivity coefficients were evaluated by the use of fixed interference method and modified separate solution method and data are given in table 3. The effect of chloride, nitrate, bromide and iodide was also investigated; the interference effect of anions on the response of hydrogen ion-selective electrode is negligibly low.

3.6 Water uptake by dummy membranes

The water uptake depends on the polarity of the plasticized membrane as well as on the aqueous solvent (solution) used to hydrate the membrane. Higher EWC

value was observed in pure water than $10^{-1} \text{ mol L}^{-1}$ NaCl solution (table 4). It is attributed to polarity of the plasticizer and coated PANI film.

3.7 Electric resistance of the membrane

The resistance of the electrode is much lower than that of a glass electrode and is favourable for electrode miniaturization. The results show that the presence of the PANI film on the membrane diminishes the ohmic resistance. In addition, it improves the response behaviour, selectivity and sensitivity of the membrane electrodes. It also facilitates the transfer of hydrogen ions into PVC matrix, by protonation or adsorption of H^+ ions from the sample solution to polyaniline. The studies have also approved the decrease in ohmic resistance with increasing of conditioning time. The data in figure 4 shows that electric resistance of PANI-coated PVC membrane was constant after 12 h conditioning in $1 \times 10^{-3} \text{ mol L}^{-1}$ HCl solution.

3.8 Analytical applications

In order to compare the applicability of the electrode response with that of the pH-glass electrodes in real sample analysis, measurements were made in complex matrices. In this evaluation, at first, the acidic solution of the car battery was diluted to a measurable pH with conventional glass electrode. On the other hand, pH of this sample was determined using the proposed electrode with no dilution. The hydrogen ion concentration found by proposed electrode was $8.3 \times 10^{-1} \text{ mol L}^{-1}$ (pH 0.08 ± 0.01). This value is in agreement with labelled value (pH 0.1). However, this favourable response should be seen with some care in the sense that the use of this electrode in complex media can occasionally lead to error due to complexation or redox effects.

The newly prepared hydrogen ion selective electrode is also compared with three different commercial glass

Table 5. Error in pH measurement by using the commercial and the new electrode.

Buffer solutions	Eutech (pH 510) ^a	Error (%)	TOA (HM-5ES) ^b	Error (%)	Micro bench (TI 2100) ^c	Error (%)	Proposed electrode	Error (%)
0.95	1.75	84.2	2.00	—	1.28	34.7	0.92	3
0.77	1.46	89.6	1.20	55.8	1.08	40.2	0.75	2.6
0.6	1.38	—	0.97	61.7	0.86	43.3	0.56	6.6

^apH range 0.00 to 14.00; pH resolution and accuracy 0.01 and ± 0.01 pH (Thermo Fisher Scientific Inc.)

^bpH range 0.00 to 14.00; pH resolution and accuracy 0.01 and ± 0.02 pH (Analytical Instruments Corporation)

^cpH range 0.00 to 14.00; pH resolution and accuracy 0.01 and ± 0.01 pH (Trans Instruments, Singapore)

pH electrodes at low pH values 0.6–0.95. Buffers in various pH (0.95, 0.77, 0.6) were prepared. Their pH was determined both with glass pH electrodes and the newly prepared pH electrode. The results are given in table 5. Here the pH values measured with the glass pH electrodes are compared with pH of buffers. Their relative errors and the error made with the new electrode are given in table 5. As can be seen and as expected, the error made with glass pH electrodes is high at low pHs. On the other hand, the new electrode can be used safely at very low pH values (0.1–1.0).

4. Conclusion

In this study, conducting polymer, PANI was coated on the PVC membrane containing ionophore kryptofix 22 DD. This enhanced the sensitivity and stability of the electrode response for determination of pH values in highly acidic media. In fact, PANI film facilitates the transfer of hydrogen ions from the sample into PVC matrix. This is done through protonation or adsorption of H^+ on polyaniline. The macrocyclic component as an ionophore introduced into the membrane increases the selectivity of the fabricated pH sensor electrode because of its inherent structure. The resistance of the proposed membrane electrode is much lower than that of a glass electrode and is favourable for electrode miniaturization. The prepared electrode was shown to have pH values near the theoretical value, in the range of pH 0.1–1 and it can be used for pH measurements in various real samples.

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