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ELECTROCHEMICAL SYNTHEZIS AND CHARACTERIZATION OF POLYPYRROLE FOR DODECYLSULFATE SENSOR MEMBRANE

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ABSTRACT

A conducting polymer, polypyrrole, has been electrochemically synthesized from pyrrole monomer using cyclic voltammetry technique in aqueous solution in the presence of HDS dopant and KNO_3 supporting electrolyte. The polymer was deposited on the surface of an Au-wire and the modified electrode obtained was then used as dodecylsulfate (DS^-) ion sensor electrode. The best performance PPy-DS modified-Au electrode conditioned in the air system without HDS or SDS solution gave linear potential response for the concentration range of $1.0 \times 10^{-5} – 1.0 \times 10^{-3}$ M, sensitivity of 54.5 mV/decade, detection limit of 1.0×10^{-5} M, and response time of 23 – 30 second. The electrode showed good selectivity towards other anions, therefore can be used to determine SDS concentration in real samples system without any change of the samples matrix.

Keywords: *polypyrrole, SDS, cyclic voltammetry*

INTRODUCTION

Polypyrrole (PPy) is one of the most studied conducting polymers because of its good electrical conductivity, environmental stability and relative easy of synthesis. Based on the molecular structure of pyrrole, PPy can be prepared by electrochemical oxidation of pyrrole in various organic solvents and aqueous media[1-3]. The electrochemical polymerization of pyrrole in aqueous solution offers the possibility for a large number of anions to be applied as dopants[4]. The formation process of PPy films on electrode surfaces was studied during the electropolymerization of pyrrole in the presence of sodium dodecylsulfate (SDS)[5-7].

An electrochemical sensor for detection of nonelectroactive cations (Li^+, Na^+ and K^+) based on the incorporation of dodecylsulfate anion into PPy by electropolymerization was prepared[8]. Alizadeh and Mahmodian use this electrode as a sensor in flow-injection analysis and in high-performance ion chromatography. Dodecylsulfate-doped PPy was synthesized electrochemically by anodic polymerization of pyrrole in the presence of SDS in aqueous solution and used as a surfactant sensor[9].

Meanwhile another type of electrode made from poly (vinyl chloride) membrane, plasticized with 2-nitrophenyl octyl ether and containing PPy and SDS was also prepared. The electrode was highly selective to dodecylsulfate anion over diverse inorganic anion. The similar type of the electrode for DBS detection based on dodecylbenzenesulfonate (PPy-DBS) and was investigated[10].

The most used technique for electropolymerization of pyrrole is cyclic voltammetry. With this technique, scanning potential range, scanning rate, and scanning current can be controlled. On the other hand, the properties of the polymer obtained from the technique depend on solution composition. Thus, by controlling the parameters of cyclic voltammetry and solution composition, the best performance of the polymer as dodecylsulfate anion sensor membrane in potentiometric analysis can be obtained.

Generally, ion selective electrodes (ISEs) require a conditioning treatment a test solution before and after being used for determination of the interest ions. This treatment is aimed to develop the membrane sensor, to increase ionic mobility in the polymer, and to release the excess of unwanted reaction products. Conditioning system influences potensial response and sensitivity of the electrode. Selecting the system is a very important aspect in development of the ion sensing electrodes.

The surfactant-selective electrodes offer an attractive potentiometric method for surfactant analysis. Potentiometric sensors offer several advantages[11-13]. The sensors have generally a large linear range because the signal is proportional to the logarithm of ion activity. Short response time makes the devices very suitable for process control and allows a high sample throughput in, for example, flow injection analysis. Moreover, the potentiometric sensors can have very small dimensions and consequently, only small sample volumes are required. The most attractive features include its feasibility, the portability of the device and preservation of the sample.

Recently, we reported the preparation of new sensor for dodecylsulfate with coated wire form electrode. In the research, electropolymerization of pyrrole was applied by using cyclic voltammetry technique in the aqueous solution in the presence of HDS dopant and KNO_3 supporting electrolyte. In this

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technique, Au-wire electrode is applied as working electrode. Electropolymerization of pyrrole and coating was done on the surface of the electrode. The voltammetric parameters, solution composition, and conditioning system of PPy-DS modified-Au electrode were studied.

EXPERIMENTAL SECTION

Reagents

All reagents used were analytical grade, purchased from Sigma. Before used, 98% (w/v) pyrrole was covered with aluminium foil and stored in the refrigerator to prevent UV degradation. Other reagents used were sodium dodecylsulfate (SDS), sodium octylsulfate (SOS), sodium dodecylbenzenasulfonate (SDBS), potassium perchlorate ($KClO_4$), potassium nitrate (KNO_3), potassium fluoride (KF), potassium chloride (KCl), potassium bromide (KBr), and potassium iodide (KI).

Procedure

Electrode preparation

Polypyrrole (PPy) synthesis and characterization were performed in a three-neck- cell using the 1 mm diameter Au wire as working electrode, 0.1 mm diameter platinum wire auxiliary electrode, and Ag/AgCl (3 M NaCl) reference electrode. A unit of Potentiostat *IdInstrument PowerLab400* model was used for electropolimerization of pyrrole by cyclic voltammetry technique.

Before electropolymerization, the surface of the Au-wire working electrode was polished on a polishing cloth with alumina slurry (0.05 μm) and then cleans with pure water. PPy-DS thin film was prepared and coated on the surface of Au wire working electrode by electropolymerization from an aqueous solution containing pyrrole (0.05 M), DS$^-$ dopant (1.0x10^{-3} M), and KNO$_3$ (0.1 M) supporting electrolyte. The electropolymerization was performed at room temperature by cyclic voltammetry technique in the potential range of -0.9 to 1.0 V with scan rate of 100 mV/sec., scanning number of 60 sycles, and a current of 2 mA. The obtained PPy-DS coated membrane electrode (CME) was then conditioned for a few days in HDS solution, SDS solution, and in air system without HDS or SDS solution (dries condition).

Potentiometric measurements

The PPy-DS modified-Au electrode was used as working electrode in junction with an Hg_2Cl_2 reference electrode. All emf measurements were carried out using the following cell notification:
Hg|Hg$_2$Cl$_2$, KCl (1M)|sample solution|PPy-membrane|Au

A pH/ions meter 420 A Orion model was used for potential measurements at a temperature of 25°C. Callibration curves were constructed by plotting the cell potential *vs.* –log C of the SDS solution for the concentration range of 1.0 x 10^{-10} – 0,1 M. Sensitivity of the electrode is determined from the linear potensial response of the curves.

RESULT AND DISCUSSION

Electrode Response

The response of PPy-modified electrode depends on the equilibrium mechanism that exists on a membrane. In a solution containing variable concentrations of DS$^-$ anion, the PPy-modified electrode shows a potentiometric response proportional to the DS concentration. According to Doblhofer's model [14, 15], electrode potential can be expressed as:

$$E = E^o + \frac{RT}{F}\ln\left(\frac{a_{poly^+}}{a_{poly}}\right) + \Delta\varphi^{'} \tag{1}$$

where E^o is a constant (a formal redox potential of a redox polymer). a_{poly^+} and a_{poly} are the activities of oxidized and reduced forms of a conducting polymer, respectively, and $\Delta\varphi^{'}$ is the potential at polymer|solution interface. In the absence of specific interactions between ions and a polymer layer, $\Delta\varphi^{'}$ can be interpreted as the Donnan potential:

$$\Delta\varphi^{'} = \Delta\varphi_D = \frac{RT}{F}\ln\left(\frac{[DS]_{poly}}{[DS]_{sol}}\right) = \frac{RT}{F}\ln\left(\frac{[C^+]_{soln}}{[C^+]_{poly}}\right) \tag{2}$$

where [DS] and [C$^+$] are concentrations of anions and cations, respectively, in the polymer (poly) and solution (soln) phases, as indicated by the corresponding subscripts. Equations (1) and (2) show that the potential of a conducting polymer modified-electrode depends on both the redox state of polymer and the ion concentration. For the same system of measurement, the electrode potential doesn't depend on a_{poly^+}, a_{poly}, E^o and [DS]$_{poly}$; these parameters remains constant. Consequently, Eq. (1) can be expressed as follows:
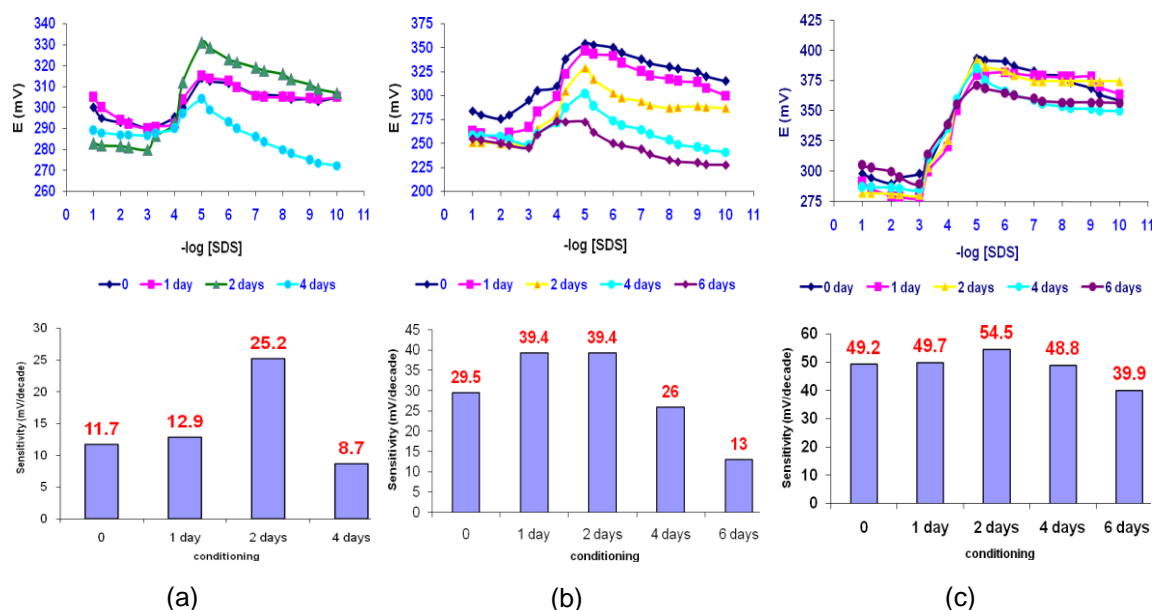
$$E = K - \frac{RT}{F}\ln[DS]_{soln} \tag{3}$$

where

$$K = E^o + \frac{RT}{F}\ln\left(\frac{a_{poly^+}}{a_{poly}}\right) + \frac{RT}{F}\ln[DS]_{poly} \tag{4}$$

In this case the potential electrode is directly depend on [DS]$_{soln}$.
Fig 1 shows potensial responses and sensitivities of PPy-DS modified-Au electrode that was prepared in

(a)   (b)   (c)

Fig 1. Potensial responses and sensitivities of PPy-DS modified-Au electrode. Conditioning system: (a) HDS solution, (b) NaDS solution, and (c) dry system.

Table 1. Response time of PPy-DS modified-Au electrode

measurement	SDS (1.0×10^{-3} M)		SDS (1.0×10^{-4} M)		SDS (1.0×10^{-5} M)	
	E (mV)	t (sec)	E (mV)	t (sec)	E (mV)	t (sec)
1	298.5	25	349.5	26	405.0	30
2	298.0	25	350.0	26	404.6	25
3	298.6	23	349.0	26	405.0	27
4	298.4	30	349.7	25	404.9	30
5	298.5	27	349.5	26	405.0	28
6	298.5	26	349.5	25	405.0	25
7	298.5	27	349.5	25	404.9	30
8	298.3	30	349.5	27	404.8	30
9	298.6	28	349.6	27	405.2	29
10	298.6	30	349.5	26	405.3	29

the pyrrole aqueous solution containing KNO_3 supporting electrolyte and conditioned in three different conditioning treatments.

Fig 1 shows that concentration range of the electrode in three difference conditioning systems was $1.0 \times 10^{-5} – 1.0 \times 10^{-3}$ M. As seen in the figure, electrode conditioned in dry system without HDS or SDS solution give the best sensitivity than another two systems. Sensitivity of the electrode conditioned in HDS solution is poor because of unstable properties of the solution, so that DS dopant in membrane lost to the solution, while the poor sensitivity of electrode conditioned in SDS solution is probably due to the unstable properties of DS dopant in the membrane.
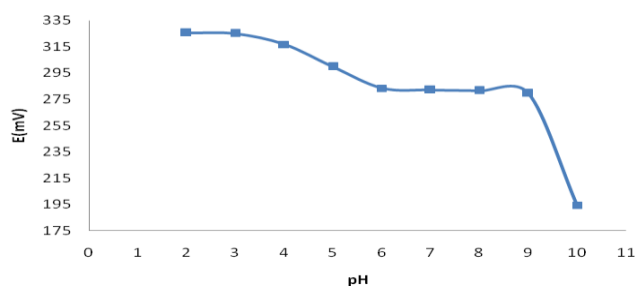
Response Time

Response time is one of the important performances of the ion selective electrodes that have to

be evaluate in development of the electrodes. This parameter correlates to electrode efficiency in analysis of real samples with potentiometric method. The short time of the response is an advantage in the analysis using ion selective electrodes. As seen in the Table 1, the proposed electrode responses potential of DS^- anions for 23 – 30 seconds. The short time of the response showed that the exchange reaction process of DS^- anions on membrane│solution interface immediately reaches equilibrium state when the electrode is immersed in SDS solution. This phenomenon demonstrated that polypyrrole as polymer conducting was proved as an effective-DS^- membrane sensor.

pH Range of SDS Solution

Effect of pH of solution on the potential response of the proposed PPy-DS modified-Au electrode (over

Fig 2. Effect of pH of SDS solution on the potential response of PPy-DS modified-Au electrode.

Table 3. Analysis of sodium dodecylsulfate in certain water samples by following standard addition method using PPy-DS modified-Au electrode

Samples	Added SDS (mol L^1) /10^{-4}	Found NaDS (mol L)/10^{-4}	Recovery (%)
aquades	1.0	1.0 ± 0.002	100.0
Tap water	1.0	1.460±0.013	146.0
Mineral water	1.0	1.500±0.018	150.0

Table 2. Sensitivity (S) and selectivity coefficient (K_{ij}) of PPy-DS modified-Au electrode to interfering ions.

	DS$^-$	DBS$^-$	OS$^-$	F$^-$	Cl$^-$	Br$^-$	I$^-$	ClO$_4^-$	NO$_3^-$
S (mV/decade)	55.0	10.9	2.6	-8.9	3.7	-2.9	6.1	7.1	15.5
K_{ij} (x10^{-5})		74.1	7.9	2.8	23.0	7.6	33.4	39.4	156

pH range of 2 to 10) in a 1.0 x 10^{-4} M SDS solution can be seen in Fig 2.

As seen, in 1.0 x 10^{-4} M SDS solution, the potential response of the electrode remains almost constant over the pH range of 6 – 9. A significant potential response change was observed for pH < 6 and > 9. At high pH, decreasing of potential response probably due to bulk concentration of OH$^-$ ions in the solution that compete with DS$^-$ ions. In other hand, increasing of the potential at low pH is probably due to the protonation of DS$^-$ ions and decreasing of concentration of anionic species in solution.[15] Therefore, the best performance for PPy-DS modified-Au electrode should be achieved in the pH range of 6 – 9.

Electrode Selectivity

In order to evaluate the selectivity of the PPy-DS modified-Au electrode to interfering ions, the potentiometric selectivity coefficient (K_{ij}) were evaluated by separated solutions method according to[16]:

$$\log K_{ij} = \frac{E_2 - E_1}{2.303RT/F} \qquad (5)$$

where E_2 and E_1 are potential responses of interfering and DS$^-$ anions, respectively. By this method, potential response and sensitivity of the electrode toward some anions in the same concentration range of DS$^-$ ion were clearly indicated. The result is summarised in Table 2.

The results showed that the electrode have good selectivity to another anions, so that it can be used to analysis DS$^-$ anion in the real samples.

Applications

The PPy-DS modified-Au electrode was used for determination of SDS in two real samples with standard addition method. The real samples were only diluted, without any other changement in the system. Table 3 shows the results obtained by the proposed electrode.

As is seen in Table 3, the real samples were significantly containing SDS surfactant.

The large of the SDS substances in tap water and mineral water were originated from some factors like the source of the water and capability of the treatment system to remove the contaminant. In These studies, those factors were not investigated. The aim of these studies was only to show the new alternative technique in determination of the contaminant.

CONCLUSION

The PPy-DS modified-Au electrode can be electrochemically prepared by cyclic voltammetry technique in the aqueous solution contains pyrrole, HDS dopant, and KNO$_3$ supporting electrolyte under optimum condition of the technique and the solution composition parameters. The best potentiometric behavior of the electrode is obtained by conditioning the electrode in the air system without HDS or SDS solution.

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