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An optical sensor for determination of low pH values based on covalent immobilization of Congo red on triacetyl cellulose films via epichlorohydrin

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ABSTRACT

A new method for immobilization of some indicators with amino groups on triacetyl cellulose beds was applied for construction of an optical sensor for measurement of low pH values. Congo red was used as a pH indicator which was immobilized covalently on triacetyl cellulose via epichlorohydrin. The response of the optical sensor to pH of the solutions was found to be 0–4.5. The effect of influencing parameters on activation of the hydrolyzed film by epichlorohydrin and also on the reaction of the activated film with the indicator was studied and they were optimized. Under optimum experimental conditions, the obtained results showed that the constructed optical sensor has a good repeatability, reproducibility, short term and long term stability (more than 9 months) and a relatively short response time (about 150 s) for a relatively wide pH range.

1. Introduction

Optical chemical sensors (optodes) have attracted the attention of many of the researchers in recent decades. Among these optical chemical sensors, the pH optodes have been studied more and they are survived actively in different areas such as, chemistry, environmental analysis, clinical analysis, process control and etc. [1–5]. The optodes have some advantages with respect to their easiness of construction, low cost, safety, remote sensing and also low electrical noise [6,7]. But they have some disadvantages such as affecting by the environmental lights, poor long-term stability in many cases, low dynamic ranges and having a limited domain of usage [8].

The dye compounds can be immobilized on a support by one of the main methods such as impregnation, doping and covalent bonding. The first and second methods are easy to do, but they suffer from numerous defects such as, swelling, dye leaching, hysteresis and inhemogenicity of the bulk [9]. The covalently immobilized dyes, do not suffer from these defects and they are more durable and have more stable signals, but this type of immobilization can only be used for some special dyes which have proper conditions. Many of the works about the covalent linking of dyes to different beds have been reported and different methods and linkers have been represented [8–16], but there is only one report on the use of epichlorohydrin as a linker for immobilization of dyes and construction of a pH optode [17–19]. According to the experimental procedure which is reported in reference 17, at first, thin transparent films of agarose are coated on the surface of the microscopic glass slides, and then epoxy activation of these slides is performed by an epichlorohydrin method [20]. Finally the desired dye or dyes are immobilized on the activated support surface. The epoxy activated agarose membranes can be used for chemical immobilization of a number of chromogenic reagents that contain at least one amino group or a strong nucleophilic agent [20].

In the present work, we have represented for the first time, the immobilization of an amino dye on triacetyl cellulose (TAC) membranes via epichlorohydrin as a linker for construction of a pH optode. Congo red (CR), as a pH indicator, was immobilized on an epoxy activated TAC support for preparation of this pH optode that can be used for accurate pH measurements in low pH regions.

2. Experimental

2.1. Reagents

Congo red, epichlorohydrin, potassium chloride, sodium hydroxide, borax, potassium hydrogen phthalate, potassium dihydrogen phosphate and disodium hydrogen phosphate were obtained from Merck chemical company. Hydrochloric acid was

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obtained from Chem-Lab chemical company. The TAC membranes were produced from waste photographic film tapes (Fomapan profi line creative). Universal aqueous pH buffer solutions were prepared according to CRC handbook (Handbook of chemistry and physics, 84th edition, Section 8, 8-43) instruction and the final pH values were adjusted by addition of 1.0 M sodium hydroxide or hydrochloric acid. Deionized distilled water was used in all experiments.

2.2. Instrumentation

The spectrophotometric measurements were performed by a double-beam Lambda 25 UV/Vis spectrophotometer. A Metrohm 827 pH meter was used for measurement the pH of the solutions.

2.3. Preparation of the sensor membranes

The transparent TAC membranes were prepared from waste photographic film tapes that were previously treated with commercial sodium hypochlorite for several seconds in order to remove the gelatinous layer. Then, the membranes were washed with tap water and distilled water, respectively. Then, the washed membranes were hydrolyzed for 24 h in a 0.2 M sodium hydroxide solution at 30 °C for de-acetylating the esteric groups and increasing the porosity of the membranes. The hydrolyzed membranes were treated with epichlorohydrin solution in a basic medium. For this purpose, 2.5 g epichlorohydrin was added to 150 ml of 1 M sodium hydroxide solution at 25 °C and mixed adequately until a clear and homogeneous solution was formed. Then, 3 g of hydrolyzed membranes was transferred into the reactor and the solution was mixed by a magnetic stirrer at 25 °C for 3 h. The activated films were immersed in 500 ml of water for 30 min and then washed completely by distilled water and finally dried at room temperature and they were cut into small pieces with about 0.04 g of weight (8 × 35 mm pieces).

For immobilization of CR on the surface of the activated films, 10 pieces of the films were transferred into a flask and 10 ml of a buffer solution (pH12) was added. Then, 0.00073 g ($\sim 1.05 \times 10^{-4}$ M) of dye was added and resulting solution stirred for 30 h at 45 °C. The immobilized films were washed with tap water and then placed in 50 ml mixture of water and methanol (80: 20 v/v) and mixed with a stirrer for 24 h at 25 °C. Finally, the films were washed with distilled water and they stored in a buffer solution (pH8).

2.4. Procedure

In spectrophotometric measurements, a raw film (Hydrolyzed TAC film) was located in reference cell and the immobilized film was placed in the sample cell.

3. Results and discussion

As we pointed out, there is only one report about the use of epichlorohydrin as a linker for immobilization of some nucleophils for construction of an optode [17–19]. Providing the use of standalone agarose membranes [17], we have to store the prepared slides in a refrigerator under a 20% solution of ethanol. Because, the agarose films are quite sensitive and they may be easily damaged, we must be careful to protect them from unwanted damages during transportation, application and also their maintenance. Another disadvantage of these films is that, they need a rigid transparent support for their better performance. This support can decrease the sensitivity due to the absorption and reflection of the light. In addition, the gradual leakage of the agarose due to its relative hydrophilicity decreases the stability of the optode. To overcome these problems, we tried to immobilize the dyes on the TAC surface via epichlorohydrin. These supports are relatively firm and they do not need a solid support. Also their solubility in water is negligible and, therefore, these films are adequately stable. For activation of the TAC membranes, an epichlorohydrin method [17,20] was used with some modifications. After hydrolyzing the films, epichlorohydrin was used as an activator. To achieve the maximum activated sites, we tried to optimize the effective parameters on the activation process.

3.1. Optimization the conditions for activation of TAC with epichlorohydrin

The effect of NaOH concentration on the absorption signal of the immobilized films is shown in Fig. 1a. As is evident in this Fig., four experiments were carried out in 0.25, 0.5, 1.0 and 1.5 M solutions of sodium hydroxide and the maximum signal was observed when the concentration of sodium hydroxide is about 1 M. The effect of epichlorohydrin concentration on the absorption signal is depicted in Fig. 1b. As is seen in this Fig., the absorption signal by increasing the epichlorohydrin concentration up to about 0.2 M increases. The higher epichlorohydrin concentrations may damage the constructed films, therefore, 0.2 M concentration of epichlorohydrin was used in the subsequent experiments. For investigation the effect of temperature on activation of the membranes, four reactions were performed at 25, 35, 45 and 55 °C. The graphical results are shown in Fig. 1c. As is obvious in this Fig., the maximum absorption signal is observed at 25 °C and at higher temperatures, the intensity of the signal decreases. Finally, for finding the optimum time of the reaction, four reactions were carried out in 1, 2, 3 and 4 h. The results are shown in Fig. 1d. As is evident in this Fig., the optimum signal is obtained in 3 h. Based on these experimental results, in the next experiments, we adjusted the temperature of the reaction at 25 °C, the time of reaction at 3 h, and the concentrations of epichlorohydrin and NaOH at 0.2 M and 1 M, respectively.

3.2. Optimization the conditions for immobilization of CR

Fig. 2a shows the effect of pH on immobilization of the dye on the slide's surface. As is evident in this Fig., the intensity of absorption signal increases when pH increases from 7 to 12 and then it decreases after pH 12. The effect of the dye concentration on the absorption signal was also investigated. For this purpose, the epoxy activated film slides were transferred into 10 ml of a buffer solution at pH 12 at various dye concentrations. The results are shown in Fig. 2b. As is seen in this Fig., the absorption signal increases with concentration of the dye up to 1.9×10^{-5} M. We used 1.05×10^{-5} M of the dye in the next experiments. For study the effect of temperature, the immobilization of the dye was performed at four different temperatures (Fig. 2c). As is evident in this Fig., the absorption signal increases with increasing the temperature, but because of the probable deformation of the films at high temperatures, we used 45 °C for the next experiments. For optimizing the time of the reaction for immobilization of CR, six experiments were carried out at different times. The graphical results are shown in Fig. 2d and as is evident in this Fig., after 30 h the intensity of the absorption signal reaches its maximum limit. According to the obtained results, we performed the immobilization reaction at the optimum conditions i.e. pH 12, 30 h, 45 °C and 1.05×10^{-5}M of Congo red concentration.

3.3. Optical characteristics of the fabricated sensors

The absorption spectra for CR in solution and also in its immobilized form at different pH values are shown in Fig. 3. As is seen in this Fig., the immobilized and the dissolved forms of the dye exhibit obvious differences both in their optical properties and also in their acid-base reactivity. Fig. 3a, shows that the dissolved CR has 2 maximum peaks at 500 nm and 575 nm. Moreover, the changes in