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Reversible pH-sensitive element based on bromocresol purple immobilized into the polymethacrylate matrix

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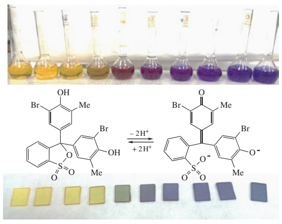
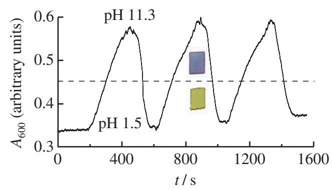
Reversible pH-sensitive element based on bromocresol purple immobilized into the polymethacrylate matrix was developed. Applications of the pH-sensitive element for continuous monitoring pH of aqueous solution were demonstrated.





Determination and continuous monitoring of pH are of importance in different fields of life and technology. Conventional electrochemical methods of pH measurements are widely used in both labs and industry. However, their application outside the lab is restricted due to known limitations such as susceptibility to electrical interferences, their size, and a rigid design. The development of optical chemical sensors extended the operational area of pH measurements far beyond labs and industry.

Detection techniques, pH-sensitive reagents and dyes, procedures and matrices for reagent immobilization used in optical pH sensor design are decsribed in a comprehensive review.[1] The sensitive element in a reagent-based optical pH sensor usually consists of a support (matrix) and immobilized chemicals. The pH-sensitive compound is typically a weak organic acid or base possessing different optical properties of its protonated (acidic) and deprotonated (basic) forms.[2] A change in optical properties depends on pH of the environment serving as the analytical signal from pH changes. This analytical signal can be measured by fluorescence and/or absorption spectroscopy. Fluorescent sensors possess a higher sensitivity in comparison with absorption ones. However, a need for the expensive equipment limits operational area of the fluorescent-based pH sensors to the laboratory. Although the analytical signal of absorption sensors in visible spectrum is evident, the precise determination of its measurable parameters also requires lab instruments. However, the opportunity of its observation without additional equipment makes absorption-based pH sensors being the optimal choice in many cases when the precise determination of pH is not necessary. Examples include smart textiles,[3,4] food packages,[5–14] *etc*. The color behaviour (coloration/discoloration or color change) indicates variations in the pH value.

Common titrimetric acid–base indicators, both individually (see refs. 5, 6, 8–10, 15–19) or as a mixture,[12,14,20] may be used for a design of the absorption sensors. The main advantages are their commercial availability and well-studied behavior for the entire pH range,[21] while their limitations in pH sensing include a narrow pH indicating range, instability in the aggressive environment, *etc*. These problems can be solved by an indicator immobilization on/into a suitable solid matrix. Various materials can be used for this purpose, *e.g*. cellulose and its derivatives (refs. 5, 12, 14, 19, 22, 23) chitosan,[16,17] hydrogel,[15] gelatin gel,[24] silica gel and sol-gel materials.[4,6–9,11,18,20]

The immobilization of pH-indicators into the matrix involves two main stages: (i) preparation of a mixture containing the dissolved matrix and pH-sensitive reagent and (ii) a transparent support coating by the mixture. Major drawbacks are usage of toxic organic solvents for the mixture preparation and a time-consuming procedure, which often is few hours long. There is an alternative approach to immobilization using a solid-phase extraction of the sensing reagent, where materials with sorption activity may be applied. A polymethacrylate matrix (PMM) is a good example of such a material. It is a specially designed one containing functional groups, which can extract both the reagent and determined analyte. PMM can be easily prepared according to the known procedure.[25] There are reported examples[26–30] of PMM applications as the support in immobilization of reagents for determination of different metal ions and species. The immobilization procedure of a reagent into PMM is simple and takes only several minutes.

In this work, PMM was chosen for immobilization of bromocresol purple (BCP) to design a pH-sensitive element. The PMM template with size of 6.0×8.0 mm and thickness of 0.60±0.04 mm was immersed into a stock solution[31] of BCP with concentration of 1.85×10^{-3} mol dm^{-3} and shaken for 3 min. UV-VIS spectra of stock solution after immobilization and BCP immobilized into the PMM are shown in Figure 1. BCP immobilization into PMM

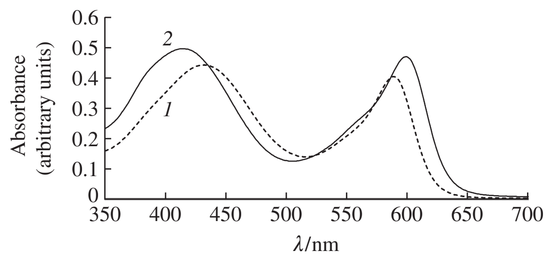


Figure 1 UV-VIS spectra of (*1*) BCP stock solution at pH 5.9 and (*2*) BCP immobilized into PMM.

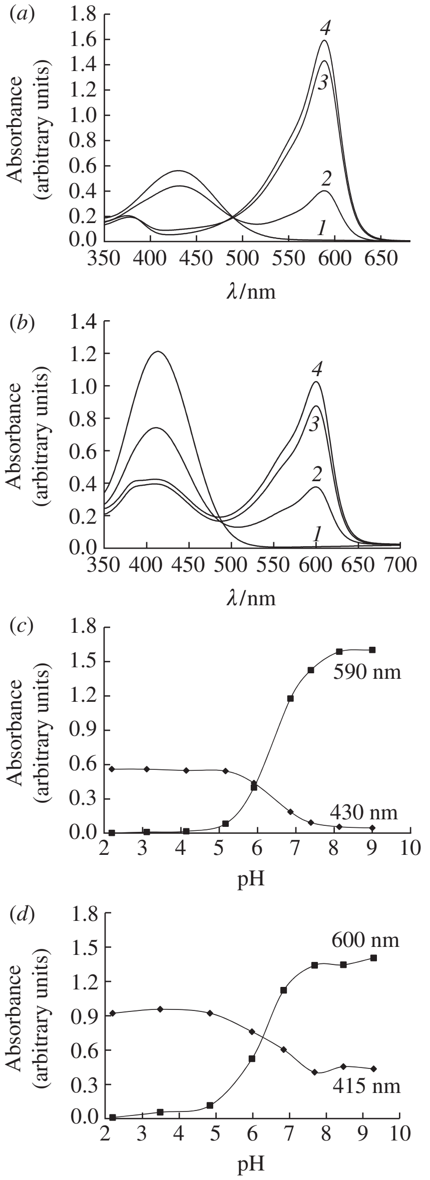


Figure 2 UV-VIS spectra of BCP in (*a*) aqueous solution and (*b*) PMM at different pH values: (*1*) 2.2, (*2*) 5.9, (*3*) 7.7 and (*4*) 9.3. Changes of absorbance maxima of BCP in (*c*) aqueous solution and (*d*) PMM *vs*. pH.

led to shifted absorbance maxima of its both basic and acidic forms (see Figure 1). The hypsochromic shift (~15 nm) was observed for the acid form, while the basic form demonstrated the bathochromic shift (~10 nm).

Optical characteristics of the pH-sensitive element were obtained for different pH values by treatment of PMM containing immobilized BCP with solutions (25 ml) of a different acidity. The UV-VIS spectra of the PMM were recorded using PMM without BCP as the reference sample. The pK_a values of BCP in aqueous solution and in PMM were calculated according to the reported method.[32] The long-wavelength region in the UV-VIS spectra was used in the pK_a calculations, the experiment being repeated three times. In each experiment, the average pK_a value of BCP was taken from pK_a values found at different pH in the range of 3.1–8.9. Figure 2 shows the comparison between the spectral characteristics of the pH sensitive matrix and aqueous solution of BCP at the different pH values. Table 1 contains equations, which describe the linear parts of curves shown in Figure 2(*c*),(*d*) with the correlation coefficient of 0.99. These equations can be used for solid–phase spectrophotometrical pH determination. The pK_a values and standard deviations are summarized in Table 2 and compared with the reported ones.

Table 1 Equations describing dependences of BCP absorbance in PMM and aqueous solution as the function of pH.

Medium	Equation	pH range
PMM	A_{600} = 0.46 pH – 2.11 A_{415} = –0.18 pH + 1.82	4.8–7.7
Aqueous solution	A_{590} = 0.64 pH – 3.25 A_{430} = –0.21 pH + 1.7	5.2–7.4

Table 2 pK_a values of BCP.

Medium	pKa	Standard deviation	Source
PMM	6.5	0.3	This work
Solution	6.43	0.13	This work
	6.494	0.003	Ref. 33
	6.40	Not available	Ref. 21

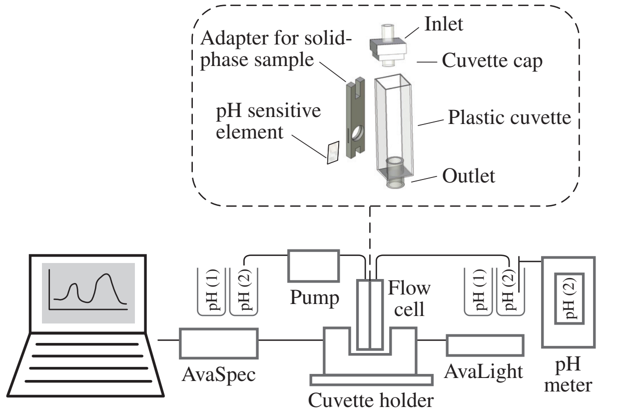


Figure 3 Schematic diagram of the measuring system set-up.

The dynamic response of the pH-sensitive element was measured using a fiber optic spectrometer (AvaSpes-ULS 2048, Avantes BV) equipped with a home-made flow cell. Flow rate in this cell was controlled by a peristaltic pump (Gilson Minipulse 3). A schematic diagram of the system set-up is shown in Figure 3.

The dynamic response was evaluated by variation of the pH value (from 1.5 to 11.3 and back) of a solution flowing through the cell. The change of the absorbance at 600 nm at different pH values was taken for the pH control. The color change from yellow to violet was visually observed. Figure 4 shows the dynamic response of the developed pH sensor demonstrating that the response time does not exceed 4 min.

Therefore, the pH-sensor based on PMM with immobilized BCP was developed. The spectral properties of immobilized BCP were evaluated. The absorption maximum shifts of the both basic and acidic forms of BCP in PMM were compared with those of the aqueous solution of BCP. The developed sensor was used for the real-time pH control of aqueous solution by spectrophotometry and also visually. The choice of PMM as matrix for immobilization

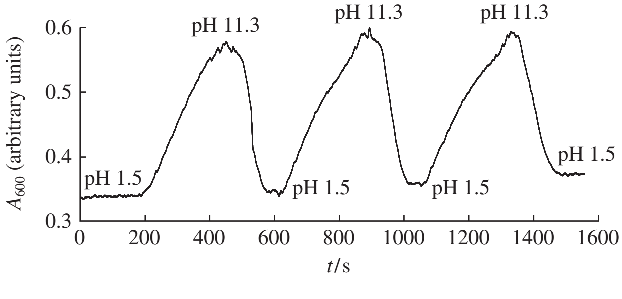


Figure 4 The dynamic response of the pH-sensor *vs*. changing the solution pH.

of the pH indicator reduced the fabrication time for the sensor down to 3 min.

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