ANALYTICAL METHODS IN CHEMISTRY AND CHEMICAL TECHNOLOGY

АНАЛИТИЧЕСКИЕ МЕТОДЫ В ХИМИИ И ХИМИЧЕСКОЙ ТЕХНОЛОГИИ

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RESEARCH ARTICLE

Shifts in the pK_a value of acid–base indicators caused by immobilization on solid substrates via water-soluble polycationic polymers: a case study of Congo Red

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Objectives. *Herein, the effects of cationic polyelectrolytes on the properties of solid substrate immobilized acid–base indicators are investigated to predict shifts in their spectral patterns and characteristics.*

Methods. *The properties of the silica gel immobilized indicator dye in a solution of the cationic polyelectrolyte were studied using automatic photometric titration in the visible region and spectrophotometry using a specialized computerized setup.*

Results. *The measured pK_a value of the immobilized dye, which had shifted by three units to the acidic region, was very similar to the pK_a value observed for the indicator in the modifying polymer solution. The observed change in pK_a of the immobilized dye and the influence of the solution's ionic strength were attributed to the local electric potential of the polymer globule. In contrast to the processes associated with covalent immobilization, the effect exerted by the solution's ionic strength on the indicator reaction diminishes, which, in turn, affects the measured values obtained.*

Conclusions. *The creation of a sensor for continuous visualization of pH levels based on Congo Red immobilized on silica gel was described. Here, a color transition was noted between pH 1 and 4. These materials can be used to monitor metal extraction processes from industrial effluents or to optimize the extraction of valuable actinides. The approach demonstrated in this work can be applied to immobilize other indicators for pH level monitoring purposes or the production of sensors for other analytes.*

Keywords: *immobilization of indicators, acid–base indicators, optical pH sensors, Congo Red, organic dyes.*

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ОРИГИНАЛЬНАЯ СТАТЬЯ

Смещение величины pK_a кислотно-основных индикаторов, вызванное иммобилизацией на твердой подложке за счет водорастворимого поликатионного полимера, на примере Конго Красного

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Цели. *Целью настоящей работы было изучение влияния катионного полиэлектролита на свойства кислотно-основных индикаторов при их иммобилизации на твёрдой подложке и установление закономерностей сдвига их спектральных и кислотно-основных характеристик.*
Методы. *Свойства индикатора в растворе катионного полиэлектролита и иммобилизованного на поверхности силикагеля изучали методами автоматизированного фотометрического титрования в видимой области, спектрофотометрии и с помощью специализированного компьютеризированного стенда.*
Результаты. *Измеренное значение pK_a красителя при закреплении на силикагеле смещается на 3 единицы в кислую область и близко к значению pK_a для индикатора в растворе модифицирующего полимера. Наблюдаемое изменение величины pK_a при иммобилизации и влияние ионной силы раствора объясняются с точки зрения влияния локального электрического потенциала полимерной глобулы. В отличие от ковалентной иммобилизации, уменьшается влияние ионной силы раствора на индикаторную реакцию, и оно может быть легко учтено при измерениях.*
Выводы. *Показана принципиальная возможность создания датчика для непрерывного визуального контроля pH на основе Конго Красного, иммобилизованного на силикагеле с переходом цвета в интервале 1–4 pH. Такой материал может использоваться для контроля в процессах извлечения металлов из промышленных стоков или для оптимизации извлечения ценных актинидов. Продемонстрированный в настоящей работе подход может быть применен для иммобилизации других индикаторов, как для обеспечения измерения в других диапазонах pH, так и для создания сенсоров на другие аналиты.*

Ключевые слова: *иммобилизация индикаторов, кислотно-основные индикаторы, оптические сенсоры pH, Конго Красный, органические красители.*

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INTRODUCTION

Acid–base indicators enable researchers to quickly and accurately control the composition of liquid or gaseous media, monitor changes related to the progress of a chemical reaction, and convert chemical information about the composition of the reaction medium into an optical signal. They are viable alternatives to electrode based indicator systems. The use of indicators in some cases may be preferable, particularly in high pressure systems or in reactions that exhibit high electrical resistivity where the use of conventional electrode systems results in unreliable readings.

Acid–base indicators usually consist of organic dyes whose molecules contain acidic or basic functional groups. Changes in the pH of the reaction environment lead to the loss or attachment of a proton by the chromophore moiety, and the proton transfer process is accompanied by observable changes in the absorption spectra (or the emission spectra in the case of luminescent systems) associated with the appearance or disappearance of certain electronic transitions in the molecule [1, 2]. These indicators are typically used as aqueous or alcohol based solutions added to the analyte sample. There are also known indicator test systems that include an indicator or a mixture of indicators adsorbed to a substrate, thereby enabling researchers to quickly determine the acid–base properties of analyte solutions [3–6]. Despite the associated benefits, there are significant drawbacks to these measurement systems, namely, the consumption of the indicator, the inability to perform continuous analysis, and the increased risk of contaminating the analyte solution. These shortcomings highlight the need to develop *in situ* reusable dye based sensors that are fixed on solid substrates [6, 7]. Such a system would avoid the issues associated with the consumption of the immobilized indicator during analysis and enable researchers to measure acidity and media composition in living cells [8]. Another potential application of these systems is for nuclear fuel reprocessing purposes, which require real-time monitoring of nitric acid concentrations to optimize the recovery of valuable uranium and plutonium actinides [9]. Furthermore, it is crucial to control the pH when extracting metals from industrial effluents [10, 11].

Although the properties of the acid–base indicator solutions have been extensively studied and documented, the immobilization may alter the observed patterns, in particular, the pK_a of a system [9, 12–14]. In light of this, the study of such regularities is invaluable. Porous microspheres [15, 16] and mesoporous membranes obtained via the sol-gel process [8, 17, 18] were previously proposed as substrates for affixing acid–base indicators as they possess a large inner surface area [16]. Unfortunately, achieving uniformed immobilization of the indicator across the entire surface of the microsphere or mesoporous materials, as well as the even penetration of the analyte [13, 19], is challenging at best. Previously, a procedure was developed to manufacture composite sensors for quantifying molecular oxygen via high-temperature phosphorescence quenching mechanisms [20]. The material consisted of mesoporous microparticles with an indicator affixed in a polymer matrix as a continuous, uniform coating. The success of that experiment prompted us to employ a similar approach to the creation of acid–base indicator systems.

In this paper, the immobilization of the Congo Red indicator in a composite matrix is studied with a particular focus on creating a flow sensor capable of monitoring the composition of the aqueous solutions. The proposed sensor would take the form of a fiber optic probe [14]. The effects of the solution's ionic strength on the pK_a value of unbound and immobilized indicators, as well as the influence exerted on the indicator in a solution of cationic polyelectrolytes used for the sorption of the indicator, were studied.

MATERIALS AND METHODS

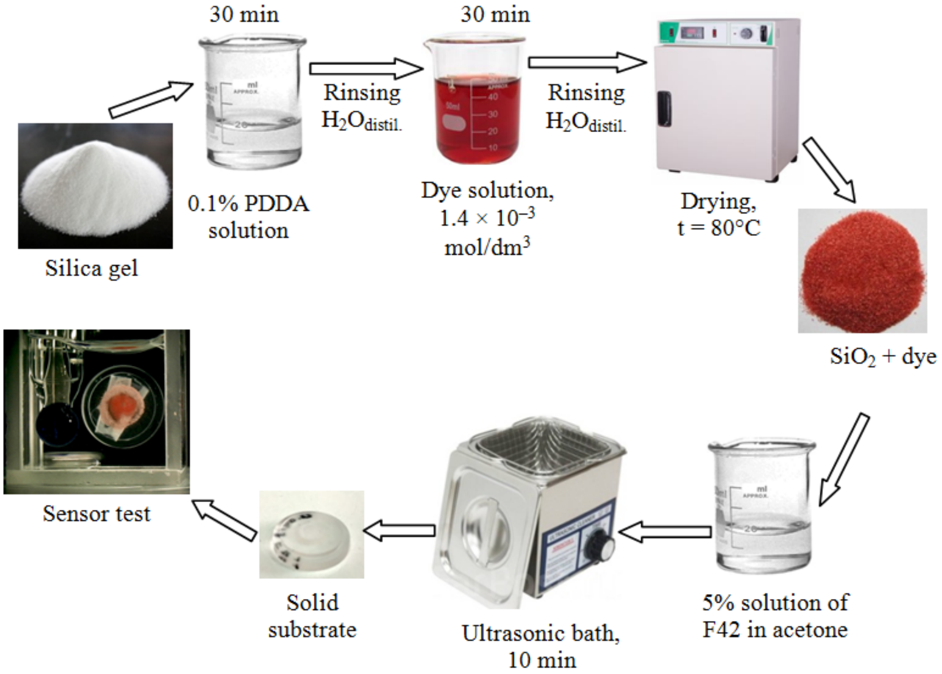
Reagents

The 4,4'-bis-(1-amino-4-sulfo-2-naphthylazo) biphenyl indicator commonly referred to as Congo Red (*LenReaktiv*, Saint Petersburg, Russia) and silica gel LS 5/40 (GOST 8984-75, *NevaReaktiv*, Saint Petersburg, Russia) were used. A solution of polydiallyldimethylammonium chloride (PDDA) with a concentration of 0.1% was obtained by diluting the initial 20% solution (*Sigma–Aldrich*, USA) with distilled water (GOST 6709-72). Fluoroplast 42 (F42, *GaloPolymer*, Moscow, Russia) was used to affix the colored silica gel particles onto the substrate. The ionic strength of the solutions was regulated using sodium chloride and potassium chloride (*LenReaktiv*, Saint Petersburg, Russia). The necessary salt solutions at the required concentrations were prepared from the initial dry reagents via a volumetric method. The appropriate acid solutions were prepared by successive dilutions of the initial solution that had been prepared from the primary standard (*Uralkhiminvest*, Ufa, Russia). All reagents were classified as "pure" or "p.a.", and were used without additional purification. All experiments were performed at a temperature of 25 ± 2°C.

The immobilization of the indicator

The immobilization of Congo Red on the SiO_2 surface using cationic polyelectrolyte was performed according to Scheme 1.

The silica gel was kept in the 0.1% PDDA solution for 30 min with periodic stirring. Next, the sample was washed repeatedly (at least 10 times) with distilled water to remove remnants of any non-adsorbed polymers before being kept for 30 min in a solution containing the indicator at a concentration of C_{CR} at 1.4×10^{-3} mol/dm^3, which had been prepared by dissolving Congo Red (0.1 g) in 100 cm^3 of distilled water. The colored silica gel was repeatedly washed with distilled water, and the completeness of processing was controlled by measuring the optical density of the wash water. Washing was considered completed when an optical density $A \leq 0.001$ was reached. Next, the silica gel was dried at $T = 80°C$ until constant weight readings were obtained. The resulting bright red powder was mixed with a 5% solution of fluoroplast 42 in acetone before being placed in an



Scheme 1. Immobilization of Congo Red on the SiO_2 surface using cationic polyelectrolytes.

ultrasonic bath for 10 min. The mixed product was then applied to substrates such as sandblasted glass or polyethylene terephthalate films using a knife coating device with a gap of 300 μm.

Conducting measurements

Determining the pK_a of the free indicators, i.e., the indicators that had not been immobilized using the above mentioned method, in aqueous solutions containing PDDA was conducted using the Titrion automatic titrator (*Econics-Expert*, Moscow, Russia) equipped with an Expert-001 pH meter combined with an ESK-10601/7 electrode (*Izmeritelnaya Tekhnika*, Moscow. Russia) and an Expert-003 photometer with a photometric cell (*Econics-Expert*, Moscow, Russia). Hydrochloric acid of various concentrations (i.e., from 1 × 10^{-3} to 2 mol/dm^3) was used as the titrant, and the dye concentration was 7 × 10^{-6} mol/dm^3. The spectral data of the solutions were measured using the small scale DT-MINI-2-GS combined spectrophotometer (*Ocean Optics*, Rochester, NY, USA). The pK_a value of the immobilized indicator was determined using the setup shown below (Fig. 1).

The color changes noted in the sample were recorded as digital micrographs using an eScope Pro DP-M17 USB microscope (*OiTEZ*, Shatin, New Territories, Hong Kong). The pH value corresponding to a given color range was determined using the Expert-001 pH meter. Data processing was conducted using in house software. The acidity of the medium was adjusted by adding the previously mentioned hydrochloric acid of various concentrations (from 1 × 10^{-3} to 2 mol/dm^3). Data was automatically acquired after the stabilization of pH meter readings.

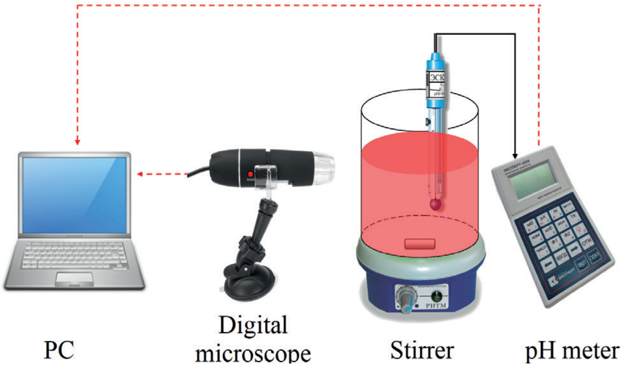
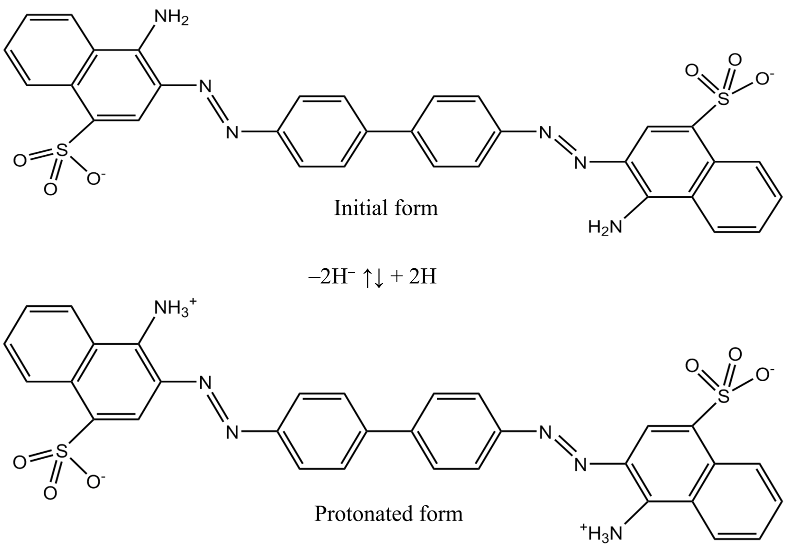


Fig. 1. Setup for determining the pK_a of the immobilized Congo Red indicator.

Generally, each pixel of a digital image represents a set of three basic colors: red, green, and blue. Since the indicator used in this study exhibited a red to blue transition in an increasingly acidic environment, the analytical signal obtained was represented as a ratio of the intensity of the red and blue color channels. Moreover, this assessment was conducted for each pixel of the image independently, making it possible to quantify local changes in pH.

RESULTS AND DISCUSSION

The mechanism governing the indicator’s reaction and the observed color changes is described in Scheme 2 [21].

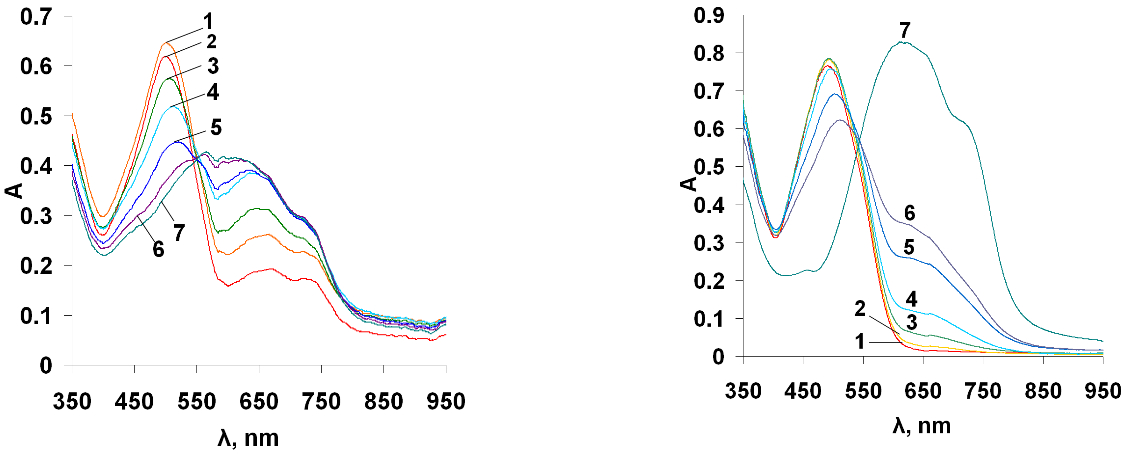


Scheme 2. The mechanism governing the indicator's reaction and the observed color changes.

The formation of an indicator–polyelectrolyte surface salt was the driving force behind the immobilization process. The Congo Red indicator molecule contains negatively charged sulfo groups that, in the presence of the polycationic polymer PDDA, resulted in effective adsorption and immobilization onto the surface of the glass substrate.

It was clear that the polyelectrolyte significantly influenced the optical properties of the indicator. Here, we noted that the optical density (A) at a particular wavelength (λ) was heavily influenced by the pH of the aqueous solution. This was exemplified in the differences observed between the spectral data obtained without and with PDDA (Figs. 2a and 2b, respectively).

In Figure 3, the maxima of the absorption peaks of the protonated (seen in blue, absorption band $\lambda_{max} = 650$ nm) and the initial (seen in red, $\lambda_{max} = 505$ nm) forms of the indicator did not shift. However, the ratio of the peak intensities of the two forms changed significantly in the presence of PDDA. The maxima of the peaks of both forms of the free indicator are changed in almost equivalent proportions, with a clearly defined isosbestic point. The intensity of the blue band (I_{blue}) in the presence of PDDA was much lower, with no clearly defined boundary between the peaks. The I_{red}/I_{blue} ratio exhibited a sigmoidal relationship with the pH of the medium (Fig. 3), and the pK_a value of the color transition was easily identified via the inflection point [22]. If the ultimate ratio of I_{red}/I_{blue} maxima for the free indicator did not exceed 3.5, then the ultimate ratio of I_{red}/I_{blue} maxima increased by almost an order of magnitude to 29 units in the presence of the polycationic polymer. In the



a

b

Fig. 2. The absorption spectrum of aqueous Congo Red solutions: (a) without polydiallyldimethylammonium chloride (PDDA) ($C_{CR} = 1.4 \times 10^{-5}$ mol/dm^3) at pH = (1) 5.55, (2) 5.01, (3) 4.52, (4) 4.23, (5) 4.09, (6) 3.87, and (7) 3.70; (b) in the presence of 0.01% PDDA solution ($C_{CR} = 2.8 \times 10^{-5}$ mol/dm^3) at pH = (1) 7.00, (2) 2.48, (3) 1.78, (4) 1.57, (5) 1.44, (6) 0.48, and (7) 0.18.

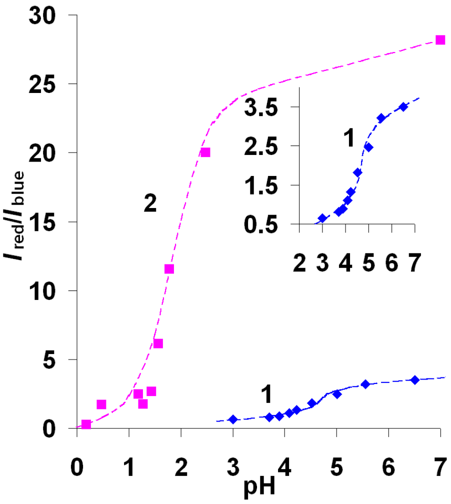


Fig. 3. Variations in the absorption intensity ratios (I_{red}/I_{blue}) of the red and blue forms of the indicator in aqueous solution based on the pH of the medium (1) without PDDA ($C_{CR} = 1.4 \times 10^{-5}$ mol/dm^3) and (2) in the presence of 0.01% PDDA solution ($C_{CR} = 2.8 \times 10^{-5}$ mol/dm^3).

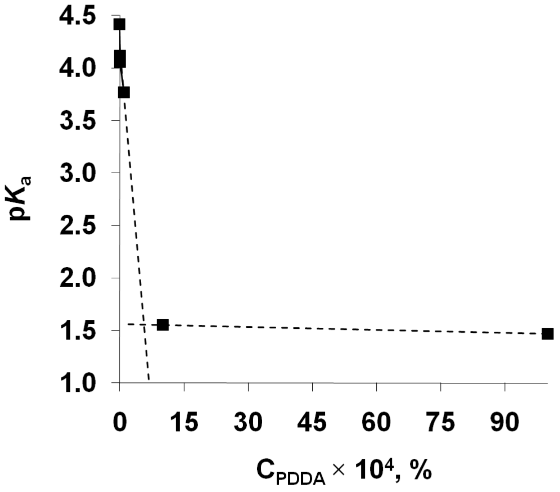


Fig. 4. The influence exerted on the pK_a value by the concentration of PDDA (%) ($C_{CR} = 7 \times 10^{-6}$ mol/dm^3).

latter case, the transition range shifted by 3 units to a more acidic region.

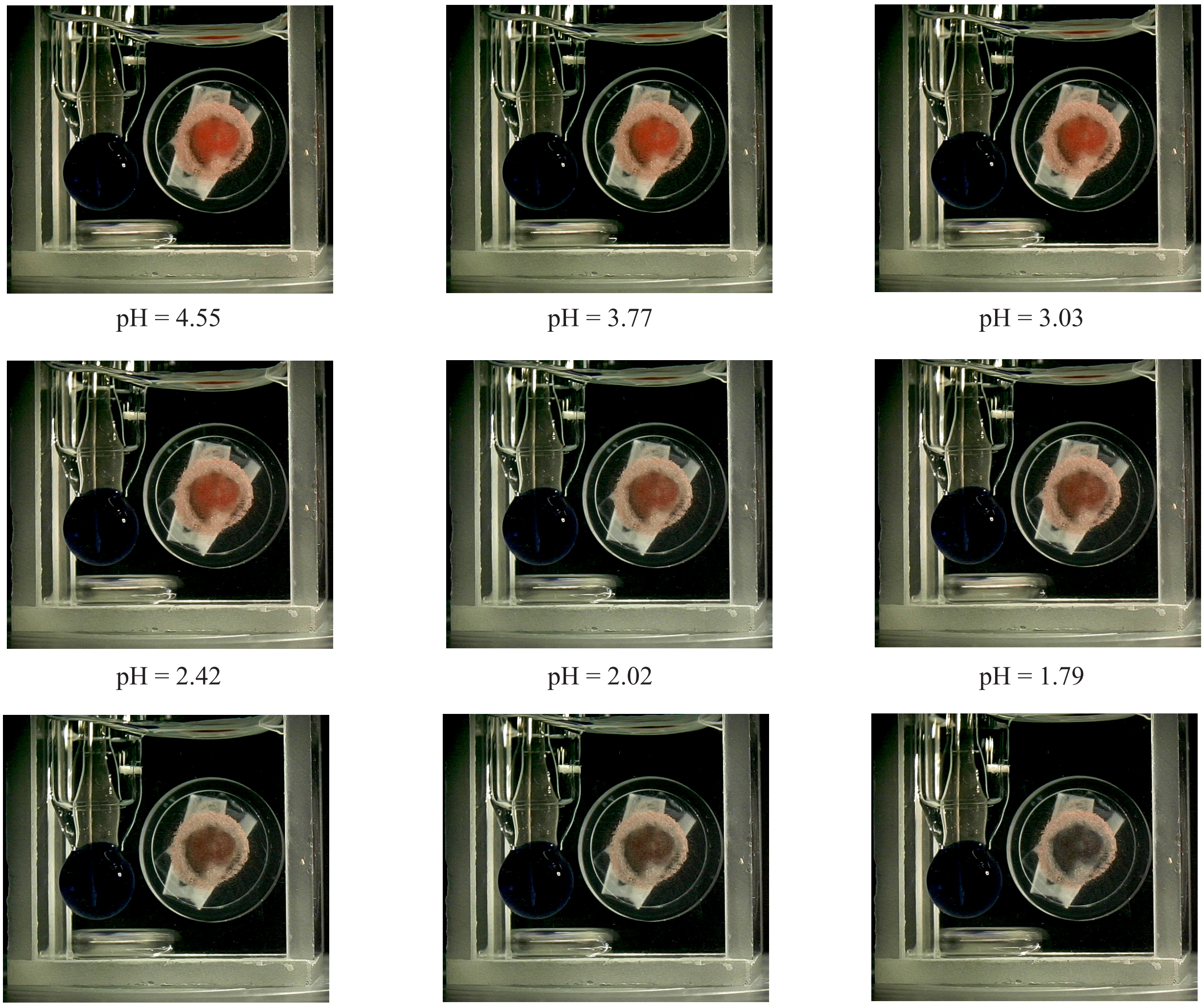
This drastic change in the pK_a value and the spectra obtained was attributed to significant shifts in the reaction equilibrium to the left due to the formation of a positively charged polymer globule around the indicator. This was exemplified by the almost complete absence of the third component (λ_{max} = 733 nm) in the spectrum that corresponded to the cationic form of the dye; this component was revealed in strongly acidic solutions [23]. In the presence of PDDA, traces of this component were visible only in extremely acidic environments at pH ~ 0 (Fig. 2b).

The pK_a values at various PDDA : indicator ratios were determined to assess the effect exerted by the polymer on dye solubilization. Here, we noted that the pK_a value decreased slightly after the addition of small amounts of PDDA. When the polymer content of the solution was 0.001 wt % or higher, the pK_a value shifted to the acidic region and equilibrium was achieved when the value was ~1.5 (Fig. 4); this observation indicated that all active sites on the polymer were occupied by the indicator. The molar ratio, which is indicated as the intersection of linear sections in Fig. 4, shows that the ratio of the structural units of the interacting charged molecules was 1 : 10 when a significant positively charged field was formed by polyelectrolyte; the latter leads to difficulties in the protonation of bound indicator molecules.

Measuring the pK_a of the solid substrate immobilized indicator is demonstrated herein. Photos of the sample at various pH values are shown in Fig. 5. In the current study, we affixed silica gel in a polymer matrix per a previously reported method [20]. Quartz fibers or glass microspheres can also be used as the carrier.

When the pH of the medium decreased, the color transition of the sample was from red to navy blue, which was a transition similar to that observed in the dye solution. The titration curves obtained after digital image processing showed the relationship between the signal intensity (represented in arbitrary units) and the pH of the medium (Fig. 6). A typical S-shaped curve was noted, which allowed us to determine the pK_a of the transition of the immobilized indicator using the inflection point [22]. The curves were reproducible during repeated titration of the sample due to the reusability of the dye; this was because the original form of the dye was firmly bound by PDDA, whereas the protonated neutral form of the dye was insoluble [23], thereby making our dye system ideal for application as a continuous optical pH sensor.

Despite numerous studies on pH sensors with low sensitivity to ionic forces [24, 25], understanding the influence exerted by the ions in the reaction medium is paramount to accurately predicting shifts in the pK_a of the indicator. A comparative study was conducted on the effect of the ionic strength of a solution on the pK_a value in an aqueous solution of the indicator, in a solution of the indicator with the addition of PDDA, and for the indicator that is immobilized on silica gel to understand how the color transition of the indicator is shifted when analyzing various natural objects, predict future color shifts, and to assess incidences of possible distortion in the readings of the sensor with the immobilized dye.



pH = 4.55 pH = 3.77 pH = 3.03

pH = 2.42 pH = 2.02 pH = 1.79

pH = 1.48 pH = 1.21 pH = 0.80

Fig. 5. Color changes in the silica gel-immobilized Congo Red indicator as a result of pH changes.

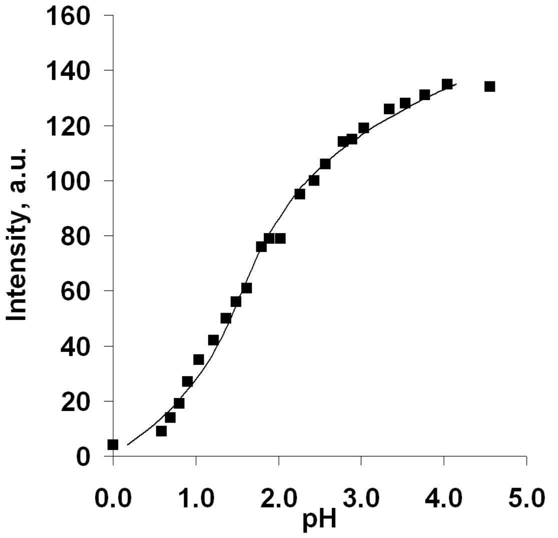


Fig. 6. Titration curve of Congo Red immobilized on silica gel.

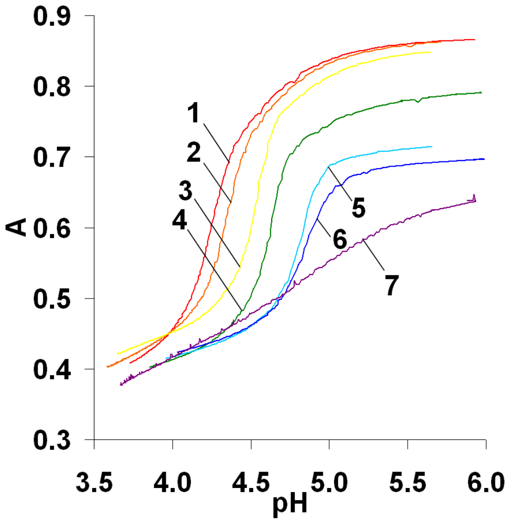


Fig. 7. Titration curves of the indicator solutions ($C_{CR} = 7 \times 10^{-6}$ mol/dm^3) at various ionic strengths, as measured in mol/dm^3, at (1) 0, (2) 0.001, (3) 0.005, (4) 0.01, (5) 0.05, (6) 0.1, and (7) 0.5.

Changes in the shape of the titration curve obtained for the indicator solution as a function of the solution's ionic strength are shown in Fig. 7. Here, we noted that in the absence of other electrolytes, the Congo Red solution underwent a color transition between pH 3.0 and 5.2, with a pK_a value of 4.3. Even though these findings were consistent with published reports [26], the shape of the titration curve changed significantly when the ionic strength of the solution increased. The associated S-shape became less pronounced at high ionic strength values, and the overall color intensity of the solution also decreased. The inflection point corresponding to the observed equilibrium constant (pK) shifted toward a higher pH (Fig. 8a).

As a result of the symmetry of the indicator molecule, its protonation can be schematically depicted as [21, 23]:

$$B^{2-} + 2H^{+} \leftrightarrow H_2B$$

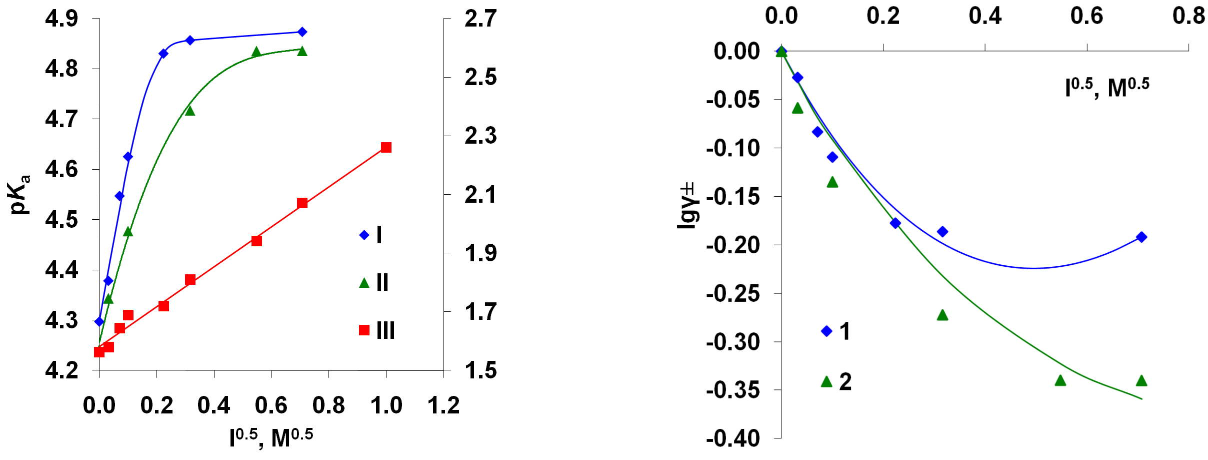
The expression for the equilibrium constant of this reaction is written as:

$$K = \frac{[H_2B]}{[B^{2-}][H^{+}]^2}$$

From the figure, it was clear that an increase in the ionic strength resulted in a decrease in the mean ionic activity coefficient ($\gamma_{\pm}$), leading to an increase in the observed constant $K_{obs} = K \times K_{\gamma}$. The calculated values for lg$\gamma_{\pm}$, which is well define by the Debye-Hückel equation, was noted as $z_1 = 2$, $z_2 = 1$, A = 0.509, B = 1, and C = 0.46 for the respective parameters (Fig. 8b). However, the addition of the polycationic polymer to the solution caused a significant deviation from the theoretical curve. A linear relationship between the shift in the pK value of the substrate immobilized indicator and the square root of the solution's ionic strength was observed even at high salt concentrations (Fig. 8a). This observation was indicative of competition between the anions of the added polyelectrolyte and the Congo Red molecules for active PDDA adsorption sites [27], which, in turn, led to the partial compensation of the polymer globule's positive charge and facilitated the protonation of the dye molecule. In contrast to the results noted for covalently immobilized dyes [28], the influence of the ionic strength of the solution on the color transition of the indicator decreased.

CONCLUSIONS

Herein, the Congo Red indicator was immobilized on a silica gel pre-treated with a cationic polyelectrolyte, PDDA. We noted that the immobilized dye retained its ability to exhibit color transitions based on the prevailing acid–base environment. A significant shift in the pK value of three pH units to a more acidic region was observed



a b

Fig. 8. (a) The relationship between the pK_a value of the Congo Red indicator and the ionic strength of (I) the aqueous solution of the indicator ($C_{CR} = 7 \times 10^{-6}$ mol/dm^3), (II) the combined 0.01% PDDA–indicator solution ($C_{CR} = 7 \times 10^{-6}$ mol/dm^3), and (III) the solid substrate immobilized indicator. (b) The mean activity coefficient ($\gamma_{\pm}$) of the ionic strength (1) without PDDA and (2) in 0.01% PDDA solution.

in the immobilized indicator due to the influence of the local polyelectrolyte's potential. Given these findings, it was clear that a sensor based on silica gel immobilized Congo Red dye could be produced for continuous visual pH monitoring via an obvious color transition between pH 1 and 4. This sensor system could prove useful during the metal extraction process conducted on industrial effluents or the optimization of the extraction of valuable actinides. The observed reduced effect of the prevailing salt environment must be taken into account since the relationship observed between the p*K* and the ionic strength of the solution is linear. The method and theories discussed in this paper can also be applied for other immobilized indicators, as a means of expanding the range and applications of these types of sensors.

Acknowledgments

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The authors declare no conflicts of interest.

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