Features of protolytic reactions in the ground and exited states in the presence of cationic polyelectrolyte

A S Mugabutaeva, A O Naumova, P V Melnikov and N K Zaytsev
Lomonosov Institute of fine chemical technologies, MIREA – Russian technological university, 86 Vernadsky Avenue, Moscow, Russia, 119454

Email: mugabutaeva@yandex.ru

Abstract. Protolytic reactions in the ground and excited states for 2-naphthol and its sulfo derivatives were studied. It was revealed that in the presence of cationic polyelectrolyte, the acidity constant of the protolytic reaction in the ground state shifts to a more acidic region. It was also found that the value of the shift depends on the number of sulfo substituents in 2-naphthol derivatives. It reaches 1.2 units for the disodium salt of 2-naphthol-3,6,8-trisulfonic acid. At the same time, no significant effect of the polyelectrolyte on the acidity constant in the excited state $pK_a^*$ was observed, and the photoprotolytic reaction proceeds in the same way as for an unimmobilized substance.

1. Introduction

Acid-base indicators are usually organic dyes, the molecules of which contain acidic or basic functional groups. Most often, indicators are used in the form of aqueous or alcoholic solutions added to the analyzed sample. Indicator test strips are also known, which include an indicator or a mixture of indicators in an adsorbed state. It is possible to quickly determine the acid-base properties of solutions by means of such systems [1-4]. The development of fluorescent indicator materials for the determination of various analytes is an actively developing scientific field. The most popular is the creation of sensors for pH [5, 6], O₂ [7], CO₂ [7-10] and other physiologically important parameters [11-15]. The phenomenon of photoinduced proton transfer has the unique properties that make it possible to measure the acidity of the medium using the ratio of bands in the fluorescence spectrum. This allows one to create a sensor without introducing a reference indicator [16].

When some substances are excited to the lower singlet excited state, their acid-base properties can change dramatically. The ability to enter into proton exchange reactions with solvent or other substances during the lifetime of an electronically excited state may appear. The mechanism of such acid-base reactions has attracted the attention of a large number of scientists since the time of the fundamental works of Weller and Eigen [17-20]. Upon excitation, some compounds become stronger bases (for example, acridine), while others, such as hydroxy- and amino-substituted aromatic compounds, become stronger acids [21]. α- and β-naphthols with an OH-group acting as a proton donor are the most typical model photoacids among a large number of known substances [22-24]. Usually, this class of molecules has an aromatic fragment and demonstrates a significant increase in acidity upon photoexcitation, which leads to the decrease in $pK_a^*$ by 5 or more units compared to $pK_a$ in the ground state. It leads to deprotonation not only in alkaline, but also in neutral and even in acidic media [25].
Earlier, the possibility of creating colorimetric pH sensor based on Congo Red immobilized on SiO$_2$ was shown [26]. To create a fluorescent sensor, it is also necessary to study the effect of PDDA on the properties of the indicator. In this work, the effect of the cationic polyelectrolyte, polydiallyldiethylammonium chloride (PDDA), on $pK_a^*$ and $pK_a$ using 2-naphthol and its sulfo derivatives as an example.

2. Experimental

2.1. Reagents
2-naphthol (N0), sodium salt of 2-naphthol-6-sulfonic acid (N1), disodium salt of 2-naphthol-3,6-disulfonic acid (N2), disodium salt of 2-naphthol-3,6,8-trisulfonic acid (N3) (Vekton, Russia) were used. Polydiallyldimethylammonium chloride (PDDA) solutions of the required concentration were prepared from the 20% stock solution (Sigma-Aldrich, USA) by dilution with distilled water (State standart GOST 6709-72). Buffer solutions with desired pH value were prepared from the original dry reagents (Na$_2$HPO$_4$ × 12H$_2$O, K$_2$HPO$_4$ × 3H$_2$O, KH$_2$PO$_4$, LenReaktiv, Russia) by the volume-weight method. The solutions of indicators with the required concentration were also prepared from the original dry reagents by the volume method. All experiments were carried out at a temperature of 25±2 °C.

2.2. Measurement technique
The pH value of the aqueous solutions of naphthol and its derivatives was monitored by means of Expert-001 pH-meter (Econi-Expert, Russia) equipped with ESK-10601/7 combined pH electrode (Izmeritelnaya Tekhnika, Russia). The concentration of the indicator was 1.57 × 10$^{-6}$ mol/dm$^3$ in all solutions. The $pK_a^*$ value was calculated by processing the fluorescence spectra of solutions measured on the Cary Eclipse fluorescence spectrophotometer (Agilent Technologies, USA). A special setup (figure 1) was used to determine the $pK_a$ value. It consisted of the pH-meter and eScope Pro DP-M17 USB microscope (OiTEZ, Hong Kong) connected to a PC running in-house software. The array of LED's with a wavelength of 375 nm was used for the solution excitation, since only deprotonated form is excited under these conditions. The investigated solution was placed in the cuvette compartment, and the image was taken automatically after stabilization of the pH meter reading. A series of solutions in phosphate buffer with pH from 5.7 to 10.3 were prepared for each indicator.

![](image.png)

**Figure 1.** A Special setup for $pK_a$ determination.

Each pixel in a digital image represents a set of three basic colors: red, green, and blue. The luminescence color of 2-naphthol and its sulfo derivatives varies from blue to blue-green, and the change in the intensity of both blue and green color channels can serve as an analytical signal. Such an
3. Results and discussions

Protolytic reactions of 2-naphthol and its sulfo derivatives proceed according to the scheme [27, 28]:

\[
\begin{align*}
\text{ROH}^* + \text{H}_2\text{O} & \quad \xrightarrow[pK_a^*]{h\nu} \quad \text{(RO)}^* + \text{H}_3\text{O}^+ \\
\text{ROH} + \text{H}_2\text{O} & \quad \xrightarrow[pK_a]{h\nu} \quad \text{(RO)}^* + \text{H}_3\text{O}^+ \\
\end{align*}
\]

Dissociation occurs both in the ground (ROH) and in the excited (ROH*) state. The first process is characterized by the value of \(pK_a\), and the second by \(pK_a^*\). In both cases, 2-naphthol and its derivatives are acting as donor molecules, and water molecules are acting as a proton acceptor.

First, a comparative study of solutions of 2-naphthol and its sulfo derivatives was carried out to determine the effect of the number of sulfo groups on their optical properties. Figure 2 shows the absorption and fluorescence spectra of the initial and deprotonated forms of N1. It can be seen that deprotonation leads to a shift of the peaks to a longer wavelength region, both in the absorption spectra and in the emission spectra. The initial form is observed in a strongly acidic medium, and the fully deprotonated form is observed in a strongly alkaline medium. A change in the pH of the medium leads to a change in the ratio of the intensities of the bands. It can be used as an analytical signal for pH determination without using an external reference dye.

The dependence of the fluorescence spectra on pH for the example of N1 and N2 is shown in Figure 3a and b, respectively. It can be seen that the ratio of the amplitudes of the peaks of the initial (\(\lambda_{\text{max}} = 357 \text{ nm}\)) and deprotonated (\(\lambda_{\text{max}} = 417 \text{ nm}\)) forms strongly changes with pH change. Similar changes are observed for the fluorescence spectra of N0 and N3. The increase in the number of sulfo groups in N0 - N3 series leads to a change in the intensity ratio of the observed peaks. As a result, the peak of the deprotonated form predominates in the N3 fluorescence spectrum.
Figure 3. The dependence of the fluorescence spectra on pH for N1 (a) and N2 (b). $C_{dye} = 1.57 \times 10^{-6}$ mol/dm$^3$.

The change in the ratio of the intensities of the peaks of the initial and deprotonated forms of the indicator is shown by the example of N2 in Figure 4. Two S-shaped sections are observed in the range of 0.5 ÷ 3.5 and 6 ÷ 11. The first corresponds to the photoinduced proton transfer reaction ($pK_a^*$), and the second corresponds to the dissociation of the molecule in the ground state ($pK_a$). Therefore, the studied indicator systems can be used in both acidic and alkaline media.

Figure 4. The change in the ratio of the intensities of the peaks of the initial and protonated forms ($I_{463}/I_{377}$) in the fluorescence spectrum of N2 solution with a change in the pH of the medium.

Upon excitation with light $\lambda_{max} = 375$ nm, only the deprotonated forms of the molecules are excited. This makes it possible to study the dissociation process in the ground state, avoiding the influence of photoinduced proton transfer. The color intensity of the solution increases (goes from almost colorless to blue-green) with increasing pH. This is shown in Figure 5.

Figure 5. The changes in the fluorescence color of N2 solution with increasing pH.

The effect of PDDA on the equilibrium constant of the deprotonation reaction in the ground state is shown in Table 1. It can be seen that the more SO$_3^-$ substituents in the molecule, the stronger is the...
effect of the cationic polyelectrolyte on the system. This indicates a specific interaction of positively charged centers with negatively charged sulfo groups. Partial or complete compensation of the negative charge occurs, which facilitates the deprotonation of naphthol derivatives.

Table 1. The dependences of the pK\textsubscript{a} and pK\textsubscript{a*} values for the indicators in distilled water and 0.05% PDDA solution.

| Number of sulfo groups | pK\textsubscript{a} \text{H}_2\text{O} | pK\textsubscript{a} \text{PDDA} | ΔpK\textsubscript{a} | pK\textsubscript{a*} \text{H}_2\text{O} | pK\textsubscript{a*} \text{PDDA} | ΔpK\textsubscript{a*} |
|------------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 0                      | 9.45           | 9.43           | -0.03          | 2.82           | 2.80           | -0.02         |
| 1                      | 8.94           | 8.29           | -0.65          | 2.61           | 2.53           | -0.09         |
| 2                      | 8.57           | 7.52           | -1.05          | 2.38           | 2.30           | -0.08         |
| 3                      | 8.13           | 6.93           | -1.20          | 1.93           | 1.99           | 0.06          |

Despite the obvious influence of the cationic polyelectrolyte on the dissociation reaction in the ground state, which facilitates an increase in the number of sulfo groups, the effect of the field formed by PDDA on the process of photoinduced proton transfer itself was not revealed. pK\textsubscript{a*} values for all studied substances practically does not change when the polymer is introduced into the solution. The most probable reason for this is that upon photoexcitation, the indicator molecule becomes such a strong acid that the influence of the local environment can be practically neglected.

4. Conclusions
By the example of 2-naphthol and its sulfo derivatives, which are typical photoacids, it is shown that the addition of a cationic polyelectrolyte facilitates deprotonation in the ground state. In the considered series, the pK\textsubscript{a} shift depends on the number of sulfo groups in the molecule. With the addition of PDDA, ΔpK\textsubscript{a} monotonically increases from 0 for 2-naphthol (n = 0) to 1.2 for 2-naphthol-3,6,8-trisulfonic acid disodium salt (n = 3). Wherein, the local charge of the polyelectrolyte, which affects the dissociation process in the ground state, does not affect the reaction of photoinduced proton transfer. The luminescent properties of the indicator lower singlet-excited state do not change in this case. This allows the use of polyelectrolytes for the immobilization of photoacids or photobases to create flow sensors for pH.

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